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Energy analysis of chemical batch plant through advanced integration of energy conversion, production system and waste management

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Abstract

The growing awareness of the society for the environment increasing the pressure for stricter environmental regulations and the increasing energy prices have modified the way chemical industry designs new processes and optimizes existing ones. In response to these challenges process design is moving towards a wider "cradle-to-gate" scope considering the interactions of the main production process with the material and energy supply chains and the waste treatment processes, from a life cycle perspective. This thesis adopts this "cradle-to-gate" scope to study the energy consumption and the life cycle environmental impacts associated with the design and operation of chemical batch plants. The thesis consists of three main blocks of increasing complexity in the modelling and design of chemical batch plants, namely (i) the accurate model-based estimation of the heating and cooling energy consumption in single and multiproduct batch plants, (ii) the optimized waste management and production planning, and (iii) the optimized waste management, production planning and heat integration.

In a first phase a detailed analysis of the energy consumption of several batch processes was performed using model-based estimations and industrial data. This analysis focuses on the modelling of the thermal losses calculated from the difference between the real energy consumption and the theoretical energy demand. The theoretical energy demand is defined based on a detailed energy balance of each unit operation using dynamic plant data. Thermal losses are determined using an empirical parametric equation. The modelling framework has been developed in previous works (Bieler et al., 2005, Bieler et al., 2004, Szijjarto et al., 2008) but was extended to several more batch operations, equipment types and energy utilities. Moreover, several methods to estimate the real energy consumption have been assessed based on valve openings regulating utility flows. This analysis was carried out in two chemical batch production buildings and a bottom-up model of the utility consumptions was built for both theoretical and real energy demand allowing the comparison with the measured consumption of the production building over several weeks. This approach has demonstrated the possibility to monitor the energy consumption of a chemical batch plant with acceptable accuracy (i.e., average relative error of 20%).

In a second phase, the waste management optimisation is addressed. A superstructure consisting of several waste treatments options was generated (i.e., including material recovery from distillation, waste-to-energy thermal oxidation, and waste water treatment). The models for the waste treatment options of the superstructure have been developed in previous works (Capello et al., 2005, Koehler et al., 2006, Seyler et al., 2005) and provide a comprehensive list of life cycle inventories including material and energy utility consumptions and pollutant emissions which are a function of the composition of waste streams. Operating constraints were added to these models to represent empirical industrial limitations for the waste treatment. A multi-objective optimisation was conducted according to financial and ecological objectives to obtain the most promising mixing of waste streams within the superstructure. Two case studies were analyzed. The first one focused on the optimisation of the waste management system independently from the chemical batch plant operation, considering a small set of typical waste streams of the chemical batch plant. It is used as a benchmark to exemplify the optimisation potential for the waste management system. The second one focused on the actual set of waste streams coming from five products divided into two production periods in a multiproduct batch plant. Different allocations of products to the two production periods were studied in the form of a scenario-based analysis. Important reductions in both objectives were demonstrated in the second case study compared to both the standard plant operation and the independent waste management optimisation (first case study). One of the main reduction potential from economic point of view is the use of waste water streams instead of fresh water to dilute streams sent to oxidation processes leading to a reduction of the total amount of waste. The dilution is necessary to fulfil the operating limitations of these treatments. From environmental point of view the distribution of streams with high salts content between oxidation processes reduces both pollution emissions and auxiliaries. The selection of the solvents in the distillation units also presents trade-offs between economic and environmental objectives.

In a third phase a more complex problem including production processes, waste treatments and utility generation was analysed. A multi-objective, multi-period problem was defined dealing with the production planning of several batch processes, the recovery of material and mixing of the resulting waste streams and the heat integration between all hot and cold streams of the production and waste treatment processes. To increase the computation efficiency, the optimisation procedure is decomposed into a “master” problem for the production planning, and two independent slave sub-problems, for the mixing of waste streams and for the heat integration, following a hierarchical approach. The effect of various optimisation parameters, such as the number of periods, the environmental impact indicator used as objective function and the influence of the real energy consumption for the processes vs. the theoretical one, has been investigated in a scenario based analysis. With respect to the influence of the environmental impact indicators, it was observed that similar Pareto optimal solutions are found in all scenarios, although the trade-off extents between optimal cost and environmental performance is different for each indicator. Therefore, an interesting conclusion is that similar future studies with emphasis on energy use could consider, for example, the less data intensive CED indicator as optimisation objective for an initial screening of high-level design decisions, without significant loss optimality in more holistic environmental impact indicators, such as the EI99.

A higher production planning flexibility (i.e. more production periods) resulted in more feasible and Pareto optimal solutions, which, however, included those of the scenarios with less periods, showing that the integrated system is not locally sensitive to this production planning parameter. Moreover, the influence of more accurate estimations for the energy demand of production processes resulted in different patterns of feasible solutions in the performance domain without however affecting the Pareto-front solutions.

Finally, it should also be mentioned that the analysis of the optimisation results, and especially the decomposition of the operation costs and environmental impacts in various categories, has provided important insights for the design of the system, e.g., the cost-environmental impact trade-offs with respect to the use of excess natural gas, the interdependencies between energy demand as a result of the production planning, incineration capacity and use of wet air oxidation, etc. These findings were not straightforward to infer on the basis of empirical knowledge. This shows the importance of systematic methods to deal with complicated systems to find the optimal solutions and not only those with only a slight improvement.

Résumé

La prise de conscience croissante de la société civile envers l'environnement, a conduit à une pression croissante pour le renforcement de la réglementation environnementale qui, avec la hausse des prix de l'énergie, ont modifiées la manière dont l'industrie chimique conçoit de nouveaux procédés et optimise ceux existants. En réponse à ces défis, la conception des procédés s'est orientée vers un champ plus large d'application, dans une approche incluant le cycle de vie ou du "cradle-to-gate" qui tient compte des interactions du procédé de production principal avec l'approvisionnement en énergie et en matières premières ainsi que du traitement des déchets. Cette thèse utilise cette approche "cradle-to-gate" pour étudier la consommation d'énergie et les impacts environnementaux du cycle de vie associés à la conception et l'exploitation de sites de production chimique batch. La thèse se compose de trois grands blocs de complexité croissante, à savoir (i) l'estimation de la consommation de l'énergie de chauffage et de refroidissement basée sur des modèles détaillés des sites de production chimique batch travaillant en mono- et multi-produits, (ii) la gestion optimisée des déchets et la planification de la production, et (iii) la gestion optimisée des déchets, la planification de la production et de l'intégration de la chaleur.

Dans une première phase, une analyse détaillée de la consommation d'énergie de plusieurs procédés batch a été effectuée à l'aide des estimations basées sur des modèles et des données industrielles. Cette analyse se concentre sur la modélisation des pertes thermiques calculées à partir de la différence entre la consommation d'énergie réelle et la demande d'énergie théorique. La demande d'énergie théorique est définie sur la base d'un bilan énergétique détaillé de chaque opération unitaire en utilisant les données dynamiques des bâtiments de production. Les pertes thermiques sont déterminées en utilisant une équation paramétrique empirique. Le cadre de la modélisation a été développé dans des travaux précédents (Bieler et al., 2005, Bieler et al., 2004, Szijjarto et al., 2008) , mais a été étendu à plusieurs procédés batch, avec des équipements différents et des utilitaires différents dans le cadre de ce travail. En outre, plusieurs méthodes pour estimer la consommation d'énergie réelle ont été évaluées sur la base des ouvertures de vannes de régulation contrôlant les débits des utilitaires.

Cette analyse a été réalisée sur deux bâtiments de production batch et un modèle "bottom-up" des consommations d'utilitaires a été construit pour la demande d'énergie à la fois

théorique et réelle permettant la comparaison avec la consommation mesurée des bâtiments de production sur plusieurs semaines. Cette approche a démontré la possibilité de suivre la consommation d'énergie d'une installation batch avec une précision acceptable (avec une erreur relative moyenne de 20%).

Dans une deuxième phase, l'optimisation de la gestion des déchets est étudiée. Une superstructure composée de plusieurs traitements de déchets a été construite (comprenant le recyclage des solvants via la distillation, le traitement thermique des déchets en énergie, et le traitement des eaux usées). Les modèles des traitements de déchets ont été développés sur la base de travaux antérieurs (Capello et al., 2005, Koehler et al., 2006, Seyler et al., 2005) et fournissent un inventaire exhaustive des consommations de matières premières et d'énergie, de même que les émissions de polluants, qui sont fonction de la composition des flux de déchets. Les contraintes d'exploitation ont été incluses aux modèles empiriques représentant les limites industrielles propres à chaque traitement de déchets. Une optimisation multi-objectifs a été réalisée en fonction d'indicateurs financier et écologique pour obtenir les mélanges des flux de déchets les plus intéressants au sein de la superstructure. Deux études de cas ont été analysées. La première a porté sur l'optimisation du système de gestion des déchets indépendamment du fonctionnement discontinu de l'usine chimique, en tenant compte d'un petit ensemble de flux de déchets typiques d'un site de production. Elle est utilisée comme point de référence pour illustrer le potentiel d'optimisation pour le système de gestion des déchets. La seconde est axée sur la gestion de l'ensemble des flux de déchets provenant de cinq procédés divisés en deux périodes de production. Différentes allocations de procédés sur les deux périodes de production ont été étudiées dans le cadre d'une analyse basée sur des scénarios définis. D'importantes réductions des deux indicateurs ont été démontrées dans la deuxième étude de cas comparée au fonctionnement standard de l'installation et à l'optimisation de la gestion des déchets sans contraintes (première étude de cas). L'une des principales réductions potentielles du point de vue économique est l'utilisation des eaux usées à la place d'eau propre pour diluer les flux envoyés aux procédés de traitement thermique permettant une réduction de la quantité totale de déchets à traiter. La dilution est nécessaire pour respecter les limites de fonctionnement de ces traitements. Du point de vue environnemental, la distribution de flux avec une teneur en sels élevée entre les procédés de traitement thermique réduit les émissions polluantes et la consommation des auxiliaires. Le choix des solvants traités dans les unités de distillation implique également des solutions contradictoires en terme d'objectifs économiques et environnementaux.

Dans une troisième phase, un problème plus complexe comprenant les procédés de production, les traitements de déchets et la production d'utilitaire a été analysé. Un problème multi-périodes a été défini traitant de la planification de plusieurs procédés batch avec dans chaque période la gestion des déchets et l'intégration de chaleur entre les courants chauds et froids (issus des procédés de production et des traitements de déchets). Pour simplifier la résolution de ce système complexe, le problème d'optimisation est décomposé en un problème maître pour la planification de la production, et deux sous-problèmes esclaves indépendants, pour le mélange des flux de déchets et pour l'intégration de la chaleur, suivant une approche hiérarchique.

Ce problème a été ensuite utilisé pour comparer différents paramètres d'optimisation tels que le nombre de périodes, le choix de l'indicateur environnemental ou l'influence de la consommation réelle d'énergie pour les procédés par rapport celle théorique. L'effet du choix de l'indicateur environnemental montre que plusieurs solutions optimales se retrouvent dans toutes les courbes de Pareto, mêmes si des solutions sont propres à chaque indicateur. Ainsi, on peut conclure qu'il est possible de traiter des problèmes d'optimisation avec l'indicateur sur la demande cumulative en énergie (CED, cumulative energy demand) comme première approche de sélection, avec comme avantage une réduction des besoins en données, sans perdre les solutions optimales que fournirait un indicateur holistique tel que l'éco-indicateur 99.

Une plus grande flexibilité dans la planification via un plus grand nombre de périodes conduit à plus de solutions optimales, incluant toutefois les solutions déjà obtenues dans le cadre d'une planification à faible nombre de période. Ceci indique que le système n'est pas sensible à la planification en tant que paramètre d'optimisation. De plus, l'influence d'une meilleure estimation des besoins énergétiques dans la production modifie l'ordre des solutions possible sans toutefois affecter les solutions du front de Pareto.

Finalement, l'analyse des résultats and plus particulièrement la décomposition des coûts de fonctionnement et des impacts environnementaux en plusieurs catégories montre plusieurs effets dans le design du système (comme le compromis de la consommation de gaz naturel en terme économique et environnementaux, les conséquences du choix de la planification sur la demande énergétique et les différentes manières d'y répondre par l'incinération, l'oxydation par voie humide ou la production de vapeur, etc.) qui ne se déduisent pas de manière directe sur la base d'une connaissance empirique. Ceci montre l'importance d'une méthode systématique pour traiter des systèmes de grande complexité et pour dépasser le choix des solutions les plus simples via une utilisation complète du potentiel de l'optimisation.

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Chapter 1

1 Introduction

1.1 Integration trend in the chemical industry

Energy plays a fundamental role in the industrial processes and the control of its consumption is one of the key factors for companies to achieve a leading status in their core activities. Besides the economic motivation for reducing energy consumption, fossil fuel based production of energy utilities is also a significant part of the environmental impact of chemical production (Capello et al., 2009, Capón-García et al., 2014, Cavin et al., 2006, Corominas et al., 1994, de Souza and Lamas, 2014, Hogland and Stenis, 2000, Marechal and Kalitventzeff, 2003, Wassick, 2009, Wernet et al., 2009). Therefore, responsible management of energy use is an important factor for industries to increase their competitiveness and act responsibly for society.

The interest in energy efficiency is not recent. Since the first oil crisis in the 1970's the energy price is one of the main indicators of the economic stability. And the chemical and petrochemical sector is strongly concerned as it represents around 30% of the global industrial energy use (Saygin et al., 2011). This had led to a systematic assessment and optimization of the energy consumption during the last three decades (Linnhoff et al., 1979, Papoulias and Grossmann, 1983a, b, c) and had influenced the development of the process design in the chemical industry (Cano-Ruiz and McRae, 1998). Initially process design was focused on the reaction and the separation operations. After the energy crisis of the 1970's the framework of the process design was extended to include the interactions with the utility systems. The main result of this heat integration is the design of heat exchangers networks in order to reduce energy consumption through heat savings. Papoulias and Grossmann (1983a) presented the application of mixed-integer linear programming (MILP) to generate automatically the superstructure for the design of chemical processes and the associated heat exchanger network. This mathematical formulation allows the solving of complex problems with a large number of streams. This system was used to solve simultaneously the design of chemical processes with its heat exchanger network (Yee et al., 1990) and demonstrate the capacity of that programming method to optimize integrated problems. Floudas and Grossmann (1986) further developed this approach for multi-periods applications. In this case, the integration problem is solved for each period with a specific heat exchanger network.

To reduce the number of possible superstructures some algorithms based on the graph theory were presented by Friedler et al. (1992b). This approach is decomposed in several steps: maximal superstructure definition including all possible solutions (Friedler et al., 1992a, 1993), selection of all feasible solutions (Friedler et al., 1992a) and comparison of solutions in order to find similarities or complementarities based on a decision-mapping method (Friedler et al., 1995).

Maréchal and Kalitventzeff (1998) studied an implicit formulation of the problem targeting the design of a whole utility system generation. This method was applied to a steam turbines network in order to define the minimum energy requirement by solving the thermal cascade based on the minimal temperature difference. This approach was then applied to several processes having different minimal temperature differences in a "Total Site" concept (Dhole and Linnhoff, 1993) and different cases studies were analyzed (Chew et al., 2013).

Following the growing awareness of the civil society for environment and the resulting regulations of the legal authorities the framework of process design was further extended to include pollutant emissions. Previously waste streams were treated in end-of-pipe operations where the objectives were to comply with discharge regulations. This approach leads to an increase of the treatment costs and to the development of more complex treatment operations with increasingly demanding regulations.

This leads to a hierarchical approach in the waste management: (i) prevention of waste generation (the first principle of "Green Chemistry" (Anastas and Warner, 1998)), (ii) recycling of materials and (iii) finally selection of waste-to-energy treatment according to waste characteristics. The integration of waste management with process design becomes more relevant as process effluents are not more considered only as inputs to end-of-pipe waste treatment systems but firstly as potential raw materials in mass integrating schemes

(El-Halwagi and Manousiouthakis, 1989) and as substitutive fuels in a downgrading cascade. The case of spent organic solvents in the chemical industry can be cited as a good example of this duality (Capello et al., 2008).

The extension of the boundaries defining the framework of process integration didn't stop at the level of pollution and energy. New fields like safety (Houssin and Coulibaly, 2011, Shariff et al., 2012, Tugnoli et al., 2012), occupational health (Hassim and Edwards, 2006, Hassim and Hurme, 2010, Pandian et al., 2013) and supply chain (Corsano and Montagna, 2011, Duque et al., 2007) are integrated in the early stages of process development.

The main objective of this extended domain of analysis is to transform the chemical production as industrial activity into a sustainable activity. Moreover, the chemical process should be designed from the beginning as sustainable. The characteristics of the design of a sustainable process can be defined as a "*design activity that leads to economic growth, environmental protection, and social progress for the current generation without compromising the potential of future generations to have an ecosystem that meets their needs*" (El-Halwagi, 2012). From this definition the three main pillars of sustainability are implied: society, environment and economy.

This means that beside the economic performance other criteria are integrated. Processes should use raw materials as efficiently as possible and prevent the production of waste or emissions that can be environmentally harmful. Energy and water use should be minimized in order to preserve resources. The process should meet all regulations about safety and health and continuous improvement systems have to be defined to ensure the application of these conditions during the whole life of the process. Including all these parameters in process design still poses a great challenge for future research.

1.2 Chemical batch plants and integration

Chemical industry can be divided into several production types (Smith, 2005):

- Commodity or bulk chemistry: chemicals produced in large quantities with a small added value

- Fine chemistry: chemicals produced in small quantities with high added value, with high purity and mainly purchased as intermediates
- Specialty chemistry: chemicals produced in small volumes with high added value, mainly mixtures of several products purchased for their effect(s). Examples are pharmaceuticals, pesticides, dyestuffs or flagrances.

These different classes of chemicals production differ on several points: bulk chemistry uses mainly continuous production mode and focus on the reduction of operating cost during process design and product life cycle tends to be important. For fine and specialty chemistry a discontinuous production mode is selected and the operating and capital costs are relatively low compared to those for bulk chemistry. Chemicals from fine and specialty chemistry have in general short life cycle and priority is given to a short time to market.
Swiss chemical industry is focused mainly on fine and specialty chemistry for geographical reasons. The country owns few natural resources and does not have a direct access to sea (Hungerbühler et al., 2013). The high added value of the chemicals produced by the fine and specialty chemistry compensates the highest cost for the transport of raw materials.
The batch or discontinuous mode is more economical for the production of small volumes because of several advantages (Smith, 2005):

- Is flexible in changing production rate by changing the number of operations performed in a defined period of time
- Is flexible in changing the products portfolio according to market demand
- Uses standardized multipurpose equipment for a variety of products in the same plant
- Is flexible in accommodating changes in final product specifications
- Allows a direct implementation from the laboratory
- Allows allocating problematic batches and products

However, there are also certain disadvantages or challenges in batch production. One of the major problems with batch processing is batch-to-batch conformity: minor changes in the production conditions can lead to deviations in the final product specifications.

Moreover, the design of a batch process is more complex because of several parameters not existing in continuous processes. One characteristic of the batch process design is the selection of equipment for each batch operation called task allocation. As the equipment is designed in a standard way it is possible to share some or all units between several processes (multipurpose plants) leading to allocation problems when those processes are running at the same time. The objective of the scheduling is to organize the processes operations in the given time frame to avoid conflicts. When the batch production requires more than several batches to fulfil an order, the production is set as campaign and the scheduling problem can be simplified by allocating one unit to only one operation creating dedicated production lines (multiproduct plants) or by including storage units with different storage policies which allow more flexibility for the use of shared units. A complete review of works analyzing scheduling for batch processes can be found in Barbosa-Póvoa (2007).
The problem of heat integration in batch processes is particularly difficult. Beside the matching problem of hot streams-cold streams in terms of heat transfer, the hot and cold streams have to be available at the same time in order to have a feasible exchange, if there is no possibility of heat storage. From this perspective, two approaches for heat integration are available:

- Direct heat exchange: Heat between hot and cold streams can be exchanged only if both streams exist at the same time. This approach is strongly dependent on the scheduling of operations (Krummenacher and Favrat, 2001).
- Indirect heat exchange: The heat from hot streams is first transferred to a heat transfer medium and stored until heat is finally transferred to cold streams, when necessary (Fernández et al., 2012).

At the beginning of heat integration in batch processes a time average model was used to estimate the potential for heat recovery and heat storage units were assumed (Stoltze et al., 1995, Vaselenak et al., 1986). This allowed the determination of the maximal heat recovery.
(Kemp and Deakin, 1989a, b, c) developed a time-dependent heat cascade analysis to overcome the time average model: the process time was split into intervals analogous to the temperature intervals used in normal pinch analysis. They showed that rescheduling of operations can improve heat recovery. Corominas et al. (1994) followed this approach and

defined an optimization tool for the best heat exchange in campaign production modifying the start time of some operations to increase, if possible, the heat exchange time or to find new possible heat exchange options.

Papageorgiou et al. (1994) studied first the simultaneous heat integration and scheduling in batch plants with direct and indirect heat transfer. Pinto et al. (2003) proposed a mathematical framework for the design of multipurpose batch plants considering the consumption of external and internal utilities and the possibility of having direct heat integration within the plant. Halim and Srinivasan (2009) presented a sequential approach that creates alternate optimal schedules in the batch scheduling. They optimized the scheduling problem and generated alternate optimal schedules, for which heat integration analysis was applied to establish the minimum utility targets. A detailed review of the heat integration in batch plants is given by Fernández et al. (2012).

This short introduction shows that a lot of effort has been made in the field of heat integration but only few works (Maréchal and Kalitventzeff, 1997, Maréchal and Kalitventzeff, 1998) included the energy utility production system in their analysis: steam and water are available and integrated in the objective function but the design of the utility generation system is excluded. The utility generation system is particularly important especially from an LCA perspective, because it is a key element in the conversion of primary energy (e.g., fuels) into energy utilities.

Parallel to the heat integration mass integration was applied in batch systems. One of the first application is the work of Wang and Smith (1995) who studied the design of mass exchange network for batch processes based on pinch analysis and focused on water minimization. The methods developed for heat integration were extended to mass integration: Foo et al. (2004) aimed to define the minimum utility using a time-dependent composition interval table adapted from the work of Kemp and Deakin (1989c). They continued the study with the design of the mass exchangers network (Foo et al., 2005b), and the possibility of storage was included by Foo et al. (2005a) simultaneously with the design of mass exchangers networks in a problem of wastewater management.

To increase the water minimization the design of the mass exchangers network was included in the scheduling of operations (Majozi, 2005). Multi-objective optimizations were conducted to analyze the effect of water minimization on production over a given period. Pareto plots for trade-off between cost and environmental impact were proposed (Erol and

Thöming, 2005), Arbiza et al. (2008) presented a multi-objective optimization framework for scheduling batch process in order to deal with environmental impact along with makespan and financial performance. Adekola et al. (2013) presented a mathematical formulation for simultaneous energy and water minimization for batch process with variable schedule. They considered only profit as objective for their optimization.

An important development was made in the case of water management but this covers only a small part of the waste management of chemical industry.

For waste management of industrial sites, Hogland and Stenis (2000) introduced an analysis based on Life Cycle Assessment (LCA), including economic and energy objectives. Their method presented the implementation of a new waste management system for an industrial site and compared the base case to the energy optimization alternative and the material recovery optimization alternative. Chakraborty and Linninger (2002) described an overall system for chemical waste treatment to define the most appropriate operations according to economic and environmental objectives using combinatorial optimization. Simplified operation models were built to calculate utility consumptions and emissions as a linear function of the waste stream compositions or flows. This superstructure aimed to support long-term operation (Chakraborty et al., 2003) and investment planning under uncertainty conditions while satisfying emission limits (Chakraborty and Linninger, 2003). In a similar approach, Cavin et al. (2001) presented a tool to optimize industrial waste treatment, including a sequence of optional and terminal operations and using cost and ecological scarcity as environmental assessment indicators. This system also handles uncertainty in waste composition and in treatment efficiency.

1.3 Objectives of the thesis

In the scope of an extended energy analysis in batch production, integration has to include process operations and waste management and look for the optimal heat integration of the whole system. The potential of this kind of integration has not yet been thoroughly investigated and can offer new opportunities especially when process integration is already used in some extent but not from an overall system point of view.

In a first aspect, the present work aims to further develop the existing methodologies created in the Safety and Environmental Technology Group at ETH Zurich to analyze energy consumption in batch plants and optimize the waste management on the basis of previously developed LCA models of the waste treatment operations. To this end:

- For the energy consumption in batch plants, Bieler (2004) has shown the application of the top-down and bottom-up modeling in energy analysis. Szijjarto (2006) extended the modelling of unit operations by integrating historical process data in the form of time-series per batch and expressed the thermal losses according to an empirical equation. However, these works studied only steam consumption in reactor units. This study applied the concept developed by Szijjarto (2006) to additional unit operations (e.g., heat exchangers, dryers, etc.) and performed the same analysis on cooling water consumption including thermal losses. As a result a method to estimate real energy consumption is proposed to overcome the lack of data measurement in an industrial plant.
- In the framework of life cycle assessment, several studies on industrial waste treatments have been previously performed (Capello, 2006, Koehler, 2006, Seyler-Jahn, 2003). At the same time waste management was analyzed by Cavin (2003). However, this last work used simplified models for waste treatment based on industrial data. The creation of a global waste management system including LCIA models is for the first time proposed in this thesis in order to analyze the waste mixing policy of a real plant and highlight the improvement potential.

In a second aspect, in collaboration with the Laboratory of Industrial Energy Systems (LENI) at EPFL, the waste management system was incorporated in a computational platform to include heat integration under diverse production scheduling scenarios. The objective here is to significantly extend the boundaries of integration and study the global optimization of the chemical plant (i.e., production units, utility generation system, and waste management).

1.4 Structure of the thesis

This thesis is structured in six chapters. After the introduction, Chapter 2 gives an overview of the different modelling, assessment and optimization techniques used in the thesis. It contains energy modelling in chemical batch plant using bottom-up and top-down approaches.

Chapter 3 focuses on a detailed analysis of the energy consumption in chemical batch plants. It presents the basic modeling framework and its significant extension in this thesis in terms of several batch operations, equipment types and energy utilities. This chapter provides the basis for the estimation of energy requirement to be used in the heat integration in Chapter 5.

Chapter 4 studies the waste management in chemical batch plants both as an independent and as an integration problem with the production planning. The potential monetary savings and reduced environmental impacts are quantified representing targets for the first level of integration between production planning and waste treatment.

Chapter 5 presents a problem of global optimization including waste treatment, production planning and heat integration of the energy streams from the three parts of the superstructure with the help of a multi-networks system.

Finally Chapter 6 summarizes the conclusions of the thesis and presents an outlook for further studies.

Chapter 2

2 State of the art and methodology

2.1 Environmental impacts and Life Cycle Assessment

The environmental assessment of a process implies the use of a metric able to provide information about its sensitivity towards environment. A first approach was the waste minimization with the use of metrics based on the mass of generated waste (Hilaly and Sikdar, 1995). The principle of these metrics is to consider wastes during the whole design procedure and not just ”patched” at the end. But mass metrics do not differentiate between the environmental impact of inert substances and highly toxic chemical and reduction of pollutant emissions has few effects if hazardous components are always released in environment. Pistikopoulos et al. (1994) proposed relative environmental impact indices for multiple categories, that is air pollution, water pollution, global warming, ozone depletion, photochemical oxidation, and solid wastes, and optimized the process for each impact category. Jia et al. (1996) presented a hierarchy of indicators which integrated the toxicity and other parameters like persistency or environmental mobility to evaluate potential toxic impacts of a substance. However, toxicity of emissions is not the unique parameter to consider in order to assess the environmental impact of a process. Grossmann et al. (1982) found that the best alternative when minimizing toxicity during process design was the one in which the production of all intermediates was carried out by suppliers. From these examples, it becomes obvious that the definition of the assessment framework for the process evaluation is critical to avoid a local decrease of the metric with a higher increase at global level.

A new type of metric was proposed by (Guinée et al., 1993a, Guinée et al., 1993b) using life cycle assessment (LCA) which evaluates a product or a process from “cradle-to-grave”, that is considering the entire life cycle of the product, including extracting and processing of raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling and final disposal. The definition of the boundaries was done with the inclusion of upstream and downstream activities related to the main process itself (Guillén-Gosálbez et al., 2008).

Several methods are available based on life cycle impact categories and characterization factors which are normalized and aggregated in order to give one final value.

A list of recent studies applying the LCA approach in process design can be found in Pieragostini et al. (2012). To this end, Guinée et al. (2011) discuss the development of a Life Cycle Sustainability Analysis framework, which would extend the scope of LCA by including other sustainability criteria (i.e. economic and social) with the help of more complex models involving several disciplines. Ruiz-Mercado et al. (2011) presents an important list of sustainable indicators which can be used to assess chemical processes. A classification of the indicators is proposed according to the GREENSCOPE methodology for the evaluation and design of sustainable processes. More reviews of works presenting LCIA results can be found in Tufvesson et al. (2013).

From application point of view a Life Cycle Assessment is composed of four steps:

1. Goal definition and Scoping
2. Inventory Analysis
3. Impact Assessment
4. Interpretation

During the goal and scope definition, the objectives of the LCA are stated and the boundaries of the considered system are defined. In the second stage, the life cycle inventory (LCI), all the emissions and extractions of single substances involved in the life cycle of the considered system are identified. In the third stage, the impact assessment, the flows of each substance from each model are calculated by the superstructure and multiplied with the corresponding impact factors of each substance. The last interpretation step includes sensitivity and uncertainty analysis: most LCIA methods are based on some assumptions especially when data is missing. The identification and the sensitivity evaluation of the data elements that contribute significantly to the environmental indicator is the important part of the interpretation work. The use of several indicators based on different methods offers a good approach to confirm the results of a LCIA analysis.

In this work, Chapter 4 sets the modeling boundaries around the main waste treatment operations excluding the utility generation system. In this case, the impact of utilities was defined according to the ecoinvent database (Ecoinvent Centre, 2010).
The inventory was performed by identifying all flows crossing the boundaries: energy, material or pollutants (see Figure 4-1 and Figure 5-1). For each flow a corresponding element in the ecoinvent database was selected to integrate its impact to the final indicator. This matching is an integral part of the models developed in this thesis and there are for some components several elements in the ecoinvent database, so a different choice can show some difference in the final aggregation process. Such an example is ethanol which can be produced by fermentation and purified with distillation or by hydration of ethylene; these two elements do not have the same environmental impact.

One of the advantages of the ecoinvent database is its ability to perform life cycle assessment according to several indicators. The list of available indicators and description about their specificities can be found in Frischknecht and Jungbluth (2007).
In this thesis three indicators are used to assess environmental impacts:

- Eco-indicator 99 (Goedkoop and Spriensma, 2001). Eco-indicator 99 is a damage-oriented method for life-cycle impact assessment, a method that integrates human health, ecosystem quality, and resources utilization and uses a weighting scheme to obtain a single total score.
- Ecological Scarcity 97 (Ahbe et al., 1990). This method focuses on the emissions to air, water and soil. The weight of each emission is determined on the basis of the current emissions situation and the political targets set by Switzerland or by international policy and supported by Switzerland.
- Cumulative Energy Demand (Frischknecht and Jungbluth, 2007). This method determines the amount of (primary) energy used during the life cycle of the studied system.

2.2 Modeling

2.2.1 Energy consumption modeling

The modeling of the energy consumption is based on the work of Bieler (2004) and Szijjarto (2008) who used several methods to analyze energy consumption in the chemical batch industry and developed some thermal losses models.

The simplest method to model the energy consumption of a process is the top-down approach (Bieler et al., 2003). This method assumes a linear relation between the number of operations or the amount of products and the total energy consumption during a defined period. To take account of the consumption of the units which are working independently of the production rate, a base consumption for the production building is added. The base consumption can be determined during the shutdown period of the production building and the linear relation between production and energy consumption has to be calculated through statistical analysis. The determination of the linear relation is easily calculated if the production rate varies in a significant way. This method can be applied to multiproducts buildings too but a regression analysis is necessary and a good estimation of the energy consumption of each process is critical to obtain the correct parameters describing the consumption of each process. These methods provide an overview of the energy consumption and a possibility to monitor the energy consumption of a process to detect deviation. But no information about the units which are the main energy consumers can be retrieved from this type of analysis or no possibility to track the origin of a deviation if an increase of the energy consumption is detected. Moreover, this method is of limited use in multipurpose production buildings with dynamic production portfolio.

A bottom-up approach can overcome these restrictions but implies access to more data in order to define an energy balance on each production unit. Once the consumption of each unit is modeled an aggregation step allows the comparison with the real consumption of the building. To be able to do the comparison, a model for the thermal losses should be added to the energy balance. Szijjarto et al. (2008) proposed an empirical model based on two different type of thermal losses: the thermal losses in the heating/cooling system of the units in charge of the temperature control and the radiative thermal losses due to the temperature difference between the production unit and the ambiance. This model was successfully tested for steam consumption in a multipurpose building and a model-based monitoring tool was developed. This tool was able to perform energy balance at very high resolution (i.e., 1-minute time intervals) on each production unit, providing the potential for aggregating at production unit level, production line level, and production building level. A detailed presentation of the principles of this model is provided in Chapter 3.

2.2.2 Waste treatment modeling

A multi-input allocation model was used to define the waste treatment models (Capello, 2006, Koehler, 2006, Seyler-Jahn, 2003). This kind of model allows the calculation of the environmental impacts of a specific product out of measurement data for a mixture of several products. To set up a multi-input allocation model, the environmental impacts which are the consumption of auxiliaries and energy carriers, the generation of co-products, and the emission of pollutants are linked to the product by their specific cause.

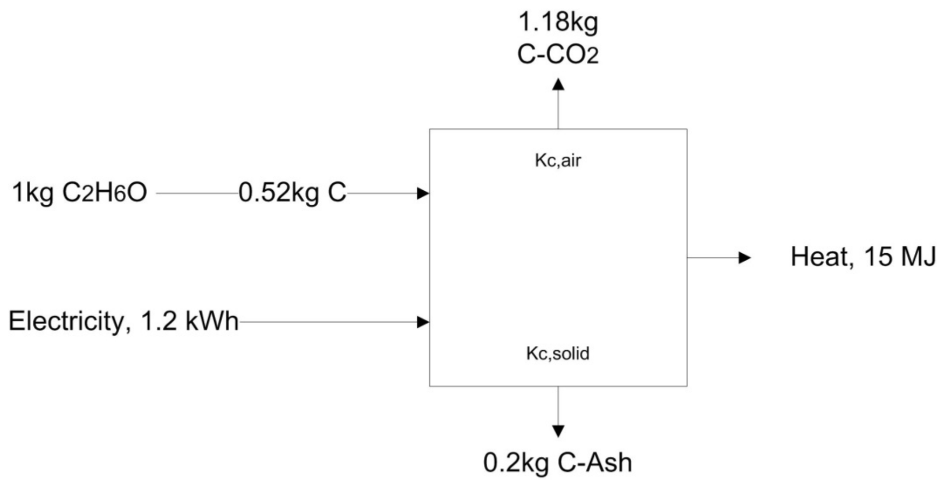

Figure 2-1 : Simplified allocation model for a combustion process where one component is decomposed into elementary flow which is then divided between different outputs according to transfer coefficients K of the model. The final outputs are converted into stable components which will be used in the impact calculation. Auxiliaries flows as well as by-products flows are added as function of mass or elementary flows responsible of their consumption or production. Only key flows defined in the LCIA database are integrated in the inventory: in this example combustion air and water emission are not represented because they have no impact in the selected LCIA method.

In the case of waste treatments, it is not possible to define the fate of each component entering the unit, so each stream sent to a waste treatment model should be decomposed into an elementary composition. Each elementary flow is then divided into one to three classes of output streams (emissions to air, to water and solid residues) according to transfer coefficients calculated from experimental measurements. Each elementary output stream is finally converted into a stable component in order to calculate its environmental impact.

2.3 Optimization

2.3.1 Pinch technology

One of the first studies for heat integration was the thesis of Hohmann (1971) but it was Bodo Linnhoff and John Flower who developed this systematic concept of the pinch technology with a first publication in (1978) when the interest in energy efficiency improvement started after the first oil crisis in the 1970's.

The method was developed in more details to include heat exchanger network synthesis in (Linnhoff et al., 1982) which became the principal vector of pinch technology dissemination in the industry. Another important development was the composite curve which offers a visual approach of the pinch technology (Linnhoff et al., 1979). The composite curves indicate the maximum energy recovery in a system described by its heat streams and have a key role in the synthesis of heat exchanger networks. Other visual applications were also derived from the composite curve to identify more clearly the possible heat exchange among a whole list of heat streams: the heat cascade table and the grand composite curve (Townsend and Linnhoff, 1983).

The concept of pinch technology was successfully applied in different cases studies along the two last decades: an overview of these works can be found in Friedler (2010).

Several extensions of the pinch technology to other process design fields have also been reported: the mass exchange networks introduced originally by El-Halwagi and Manousiouthakis (1989) for the extraction of an undesirable component in coke-oven gas using different process streams with some concentration of the impurity, the water pinch analysis presented by Wang and Smith (1994) who analyzed the wastewaters of a petrochemical plant and synthetized a wastewater treatment system to reduce the use of fresh water by transferring pollutants between water flows of different qualities before treatments, the supply chain problem by Singhvi et al. (2004) to find the bottleneck in material transportation by comparing a production curve and a demand curve in order to

minimize the final inventory and finally the total site heat integration studied by (Perry et al., 2008) to integrate the heat between different processes in an industrial site and some residential and commercial energy users and to size the heat utility generation system needed to fulfil the final demand not covered by the possible heat exchange.
A survey of the most recent publications in the field of the pinch technology and its various applications can be found in Klemeš and Kravanja (2013).

In order to start the Pinch Analysis the necessary thermal data must be extracted from the process. This involves the identification of process heating and cooling duties which are characterized by four parameters: input temperature, output temperature, minimal temperature difference for a feasible heat transfer and heat capacity flowrate (mass flowrate of a stream times its specific heat capacity). Hot streams are defined with an output temperature lower than the input temperature, cold streams as the inverse.
Once all streams are identified, the construction of the composite curve is possible. Composite curves consist of temperature-enthalpy profiles of heat availability in the process (hot composite curve) and heat demands in the process (cold composite curve) together in a graphical representation. The construction of the hot composite curve involves the addition of the enthalpy changes of the streams in the respective temperature intervals (see Figure 2-2).

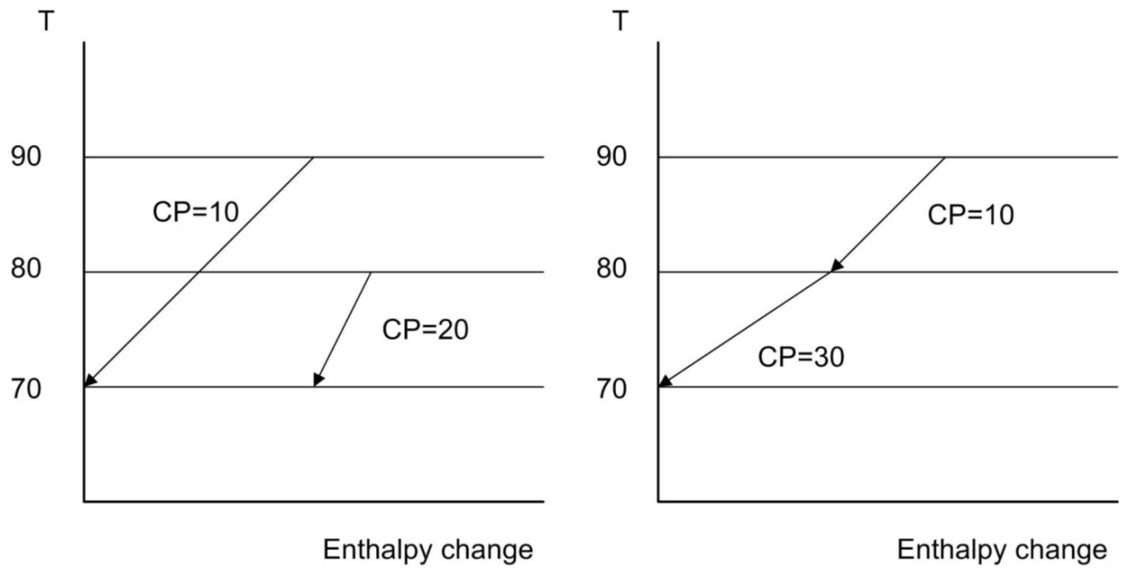

Figure 2-2 : Construction of the hot composite curve from two hot streams. CP is the heat flow per degree and is the result of the multiplication of the mass flow with the heat capacity.

The composite curves provide a counter-current picture of heat transfer and can be used to indicate the minimum energy target for the process. This is achieved by overlapping the hot and cold composite curves, as shown in Figure 2-3, separating them by the minimum temperature difference DT.

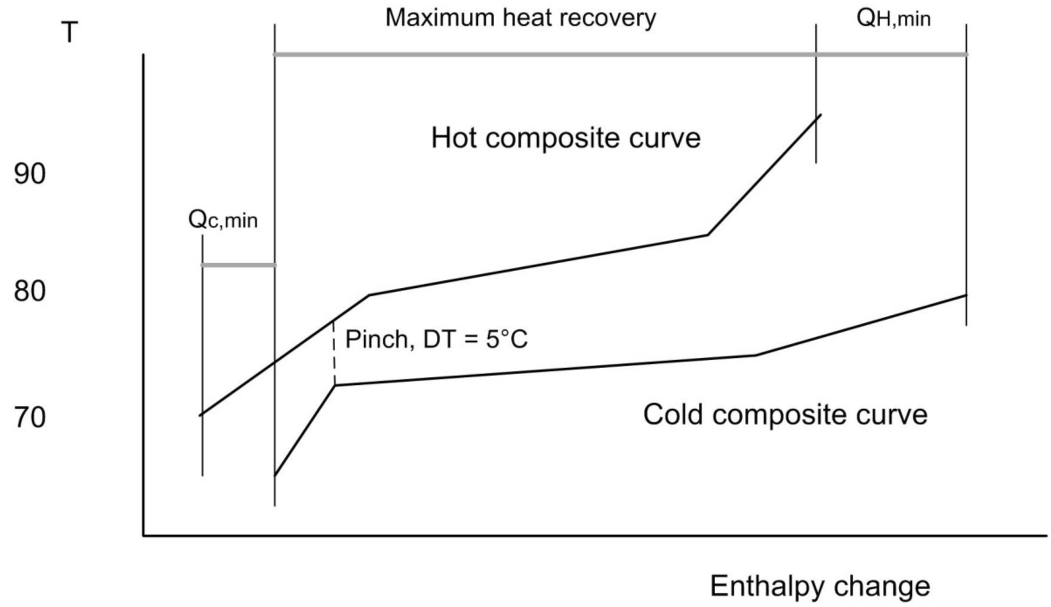

Figure 2-3 : Graphical use of the hot and cold composite curves to determine the maximal heat recovery as well as the minimum hot utility ($Q_{H,min}$) and the minimal cold utility ($Q_{C,min}$) requirements. DT is the pinch point, the minimal temperature difference to ensure a feasible heat transfer.

From the comparison of the composite curves the maximal heat recovery can be defined and the minimal amounts of the hot utility and cold utility can be calculated. These amounts are then used to design the units of the utility generation system in Chapter 5.

The solution of the heat integration is solved by a minimization of the utilities cost. If the heat exchanger network is included the investment cost of the equipment can be included in the optimization. The problem is often defined as linear even if some elements of the problems lead to non-linearities, such as the temperature dependency of the heat capacity and the heat transfer coefficients. The assumption of the linearity is still a good approximation for relative small changes of temperature during the heat transfer. The mathematical formulation of this heat integration problem is given in 5.2.3 as part of the mathematical description of the global system.

2.3.2 Modelling and optimization platform

Optimization processes were performed on the computational platform OSMOSE. OSMOSE was developed at the Laboratory of Industrial Energy Systems (LENI) of EPFL. This platform was created to solve energy systems synthesis by using different types of software in a common environment.

The key elements of this computational environment are the long list of modules describing the various technologies of the energy industry developed by the LENI (Bolliger, 2010). Each module is defined as a black box and can be provided in different programming languages (Matlab, Aspen, Vali,…) compatible with the platform. The connection to the rest of the platform is done with the help of a standard interface which allows the transfer of information between the models and the rest of the computational system. A problem is composed by a list of models handled by the optimization platform which defines their evaluation order according to the different inputs/outputs of the models and creating an explicit superstructure (see Figure 2-4).

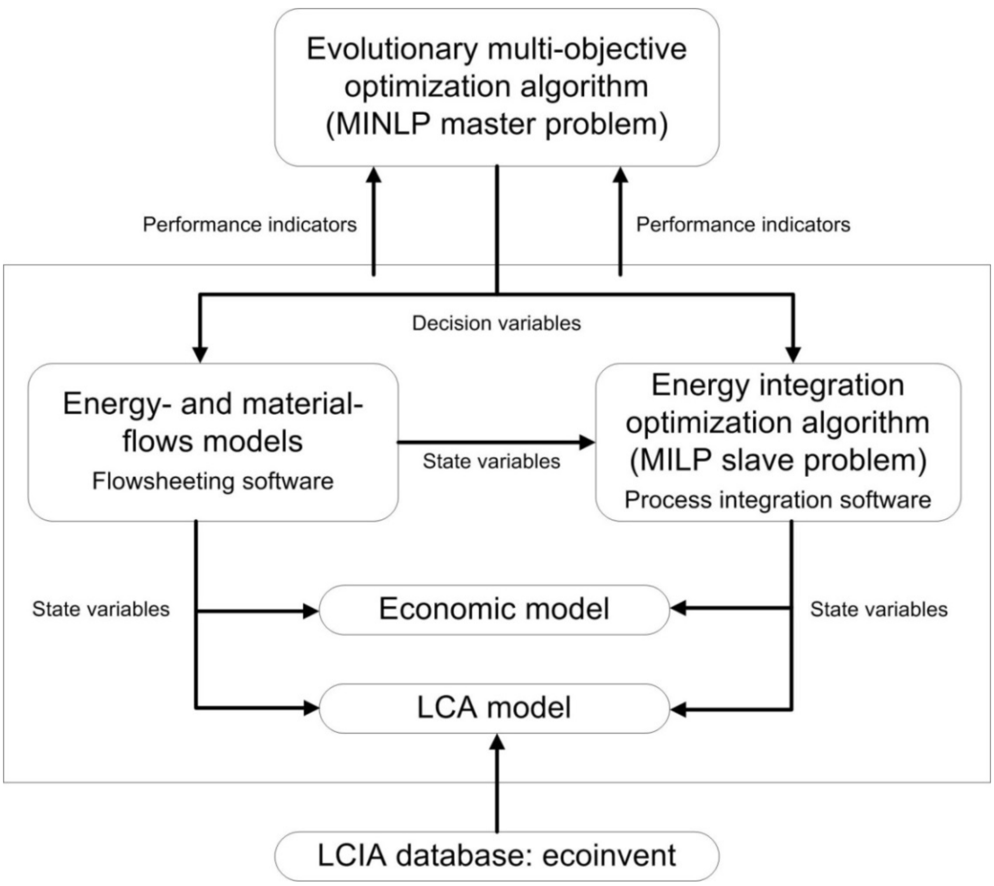

Figure 2-4 : Scheme of OSMOSE platform with data flows between the main computing elements.

One of the most interesting tools of OSMOSE is its multi-objectives evolutionary algorithm MOO (Multi Objectives Optimizer). This optimizer has proven its ability to manage in an efficient way the generation and the ranking of its variables populations in order to converge towards feasible solutions and to analyze different groups of solutions at the same time by using a clustering approach (Leyland, 2002, Molyneaux, 2002).

Another advantage of the platform is the existence of a series of tools which allow several performance evaluations: an LCA module connected to the LCIA database ecoinvent, a heat integration module (with its own MILP solver) and a module for economic calculation. If the models are well defined, the use of these tools can be activated by a single option in the definition of the problem at the beginning, leaving to the user the choice of the multi-objective dimensionality.

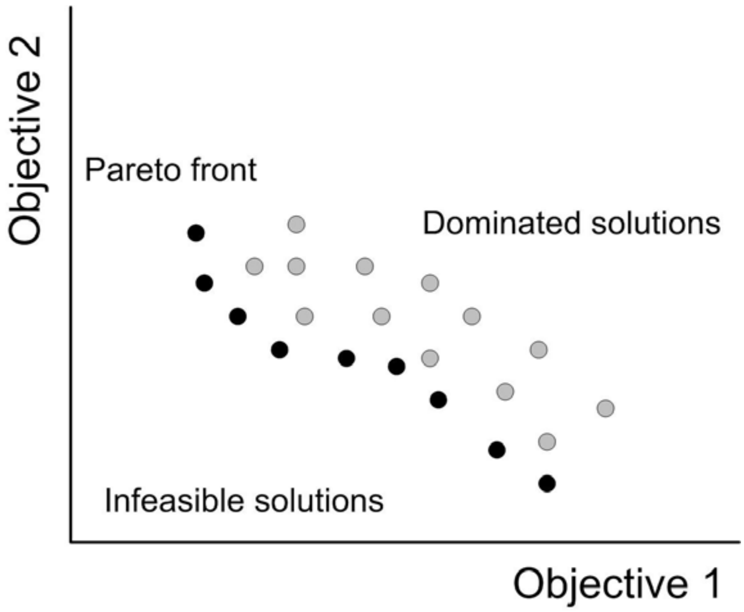

Figure 2-5 : Example of Pareto front in a multi-objectives optimization with 2 indicators to minimize, the black points are solutions defining the Pareto front. The grey points are dominated solutions.

Working with different targets implies multi-criteria assessment and multi-objectives optimization techniques to be able to analyze trade-offs between solutions in the design space and finally reach Pareto-optimal solutions. The visualization of these solutions is provided by the Pareto front which is described by solutions which are non-dominated in at least one objective (see Figure 2-5). Without specific preferences between the objectives all solutions in the Pareto front are equally optimal.

Chapter 3

3 Energy analysis of utilities consumption in batch chemical production

3.1 Introduction

Energy consumption in chemical industry gained attention as important financial parameter after the oil crisis in the 1970s motivating the development of systematic methods in order to use energy utilities more efficiently (Linnhoff et al., 1982). Nowadays energy management keeps playing a crucial role not only for economic but also for environmental reasons, mainly due to feedstock depletion and greenhouse gas emissions associated with an energy mix typically consisting of oil and natural gas for chemical industries. It is therefore not surprising that in parallel with efforts for improving the efficiency of energy production systems and increasing the part of renewable energy sources in the composition of the energy mix (Council of the European Union, 2006), a more efficient use of energy remains a key objective for sustainable chemical process design. This has been already identified in scientific studies discussing methodological issues in the definition of energy efficiency indicators (Patterson, 1996). Moreover, the interest in product and process specific energy consumption is growing with the application of life cycle assessment to process engineering (Burgess and Brennan, 2001). Most of the environmental indicators integrate energy use in the calculation and some of them are actually only focused on energy, like for instance the cumulative energy demand as life cycle impact assessment metric (Huijbregts et al., 2010). Moreover, the comparison between results of different assessments shows that energy, especially from fossil sources, plays an important role in environmental impact (Capello et al., 2009, Wernet et al., 2010).

This motivation for better use of energy has also reached the batch chemical industry where energy consumption analysis and optimization were neglected due to more important cost factors affecting its production portfolio typically comprising high-value-added products, like specialty chemicals and pharmaceuticals. For instance, optimal use of raw material often comprising expensive complex reactants, process flexibility in multiproduct/multipurpose batch plants for meeting constantly changing production requirements and development of standardized procedures (e.g., Good Manufacturing Practices, Six-Sigma Strategies) enhancing product quality and process stability are some of the economically driven incentives that have traditionally monopolized the interest of design and retrofitting practices (Barbosa-Póvoa, 2007, Moreno et al., 2009, Simon et al., 2007). On the other hand, waste treatment management has been the major industrial concern for reducing the environmental impact (Jödicke et al., 1999, Stefanis et al., 1997, Young et al., 2000).

Nevertheless, several methods have been developed, mainly in academic environment, to save energy or to select the less energy intensive process in batch production: heat integration based on pinch analysis with energy storage (Krummenacher and Favrat, 2001), heat integration coupled with simultaneous consideration of production scheduling (Adonyi et al., 2003) and rigorous modeling of mass and energy inventories involved in batch processes for comparison between different process alternatives (Van der Vorst et al., 2009). All these methods aim to reduce the total energy consumption of the production system and assume an optimal energy use at unit level with negligible losses. However, studies focusing on analysis of energy efficiency in batch operation have demonstrated that thermal losses can represent up to 50% of the total energy consumed in a unit operation (Bieler et al., 2004). In this direction, specific equipment design was proposed to optimize the energy use in chemical reactors (Phillips et al., 1997) and detailed studies of energy consumption in specific unit operations are available (Carvalho and Nogueira, 1997, Lampret et al., 2007, Simpson et al., 2006). These models provide a lot of information about different forms of energy transfer and offer interesting saving potentials but in return need a large number of input values and accurate measurements. As these data are not typically available in an industry characterized by a high turnover in the product portfolio, intermediate solutions describing in sufficient detail various unit operations in chemical batch plants and at the same time requiring easily accessible data are necessary.

In this context Bieler et al. (2004) applied a “bottom-up approach” for modeling energy consumption at unit operation level based on standard data from process step procedures (PSP) describing the most important operating conditions. Their models comprised energy balances for each process step and also included estimation of thermal losses due to free convection and radiation from the equipment surface where a unit operation takes place. With this approach it was possible to determine operations consuming large amount of energy utilities and therefore offering the most promising saving potential. Moreover, the aggregation of the energy consumption for all unit operations of the batch plant facilitated the estimation of the overall energy utility consumption, which was validated with available measuring devices at plant level. This approach was proven to be more accurate compared to “top down approaches” that try to establish empirical correlations between overall energy consumption and production volume (Bieler et al., 2003, Vogt, 2004). However, using only PSP standard data for modeling results in low resolution for the calculation of the energy use and does not allow a good representation of peak consumption.

Szijjarto et al. (2008) improved the methodology of Bieler (2004) in two ways. First, a more detailed model for thermal losses was developed. This model completed the loss term due to temperature difference between process conditions and the ambiance with an additional loss term capturing the inefficiencies of the energy transfer from the heating/cooling system. This new term depends on the rate that the energy is provided and on characteristics of the equipment and the heating/cooling system. The form of the functional relationship was based on detailed steam consumption analysis in multipurpose batch plants, while the parameters of this functional relationship were fitted to plant data for various types of equipments and heating/cooling systems. The second improvement was the use of dynamic process data to calculate the energy balance of each operation instead of static PSP standard data. These two new features increased the model accuracy, reaching approximately 10% modeling error at unit operation level, and also provided information about inefficient operations at a higher resolution (e.g., up to 1-min time interval).

The present study extends the methodology of Szijjarto et al. (2008) in various aspects. First, new types of equipments are analyzed including reactors of different sizes, various types of heat exchangers and dryers, unlike Szijjarto et al. (2008) whose work concentrated only on reactors. Then, two more utilities are considered as energy carriers, that is, not only steam but also cooling water and brine consumption are included in the energy efficiency analysis. For fitting and validating the thermal loss models various equipment and utility specific approaches are applied depending on data availability. When no direct measurements of the energy utility consumption are available for a specific equipment–utility pair, two calibration procedures are applied: a direct approach based on control valve opening and portable flowmeter devices and an indirect approach using multivariate regression analysis between individual control valve opening and aggregated energy utility consumption from available flowmeters at plant level. Moreover, validation of the bottom-up models under the extended conditions described above is carried out from unit operation and production line up to plant level offering perspectives for energy monitoring and management. Finally, by enriching the list of thermal loss model parameters for various equipment–utility pairs, it is aimed that gradually the need for fitting will be decreased and will be substituted by suitable algorithmic approaches matching equipment–utility characteristics with thermal loss parameters.

The rest of the paper is structured in the following way. In section 3.2, a three-step methodology for development and validation of the bottom-up energy utility consumption models is presented. It comprises determination of the real utility consumption for each unit operation of the plant (Step 1), then modeling of the theoretical energy demand and fitting of the equipment–utility specific parameters for the thermal loss terms (Step 2), and at the end validation of the models at unit operation, production line and plant level (Step 3). In section 3.3, a short description of the case study plant and its special characteristics regarding type of equipments and energy utilities is provided, and in section 3.4 the results of the application of the three-step energy modeling methodology to the case study plant are systematically presented for every individual step. The discussion and conclusions mainly focus on the applicability of the methodology and its accuracy at different aggregation levels and types of energy utility and equipment typically used in chemical batch plants.

3.2 Modeling approach

The ultimate goal of the bottom-up modeling approach followed in the present study is to estimate the overall energy utilities consumption of a chemical batch plant through modeling of the utilities consumption at unit operation level and subsequent aggregation. For the success of this approach at plant level, it is crucial to develop accurate models for each unit describing not only the theoretical energy demand but also the associated energy losses. This efficiency of energy use at unit operation level may also reveal interesting saving potential and motivate further analysis. The development and validation of the bottom-up models is a three-step procedure described in the following paragraphs.

3.2.1 Step 1: Utility consumption at unit operation level

In the absence of flowmeters measuring energy utility consumption in each equipment, which represents a typical case even in modern chemical batch plants, an estimation of the utility consumption can be made using the opening of control valves that regulate the utility flows. This information is recorded for all control valves in the IT system of the building for safety purposes. The recorded data are typically available as percentage of the total valve opening which has to be converted into a mass or volumetric flow rate for further calculations.

The flow through a control valve depends on the following parameters: characteristics of the valve, physical properties of the fluid and characteristics of the installation on which the control valve operates. Control valves can be divided into three main types on the basis of their inherent flow characteristic: linear, quick opening and equal percentage. The inherent flow characteristic is specified by the sensitivity of the flow rate change to the valve opening change (Spirax-Sarco, 2007). Another important valve characteristic is the flow factor K_{vs} which represents the flow rate of water at a temperature between 5 and 40 °C for a fully open valve with a pressure drop of 1 bar across the valve. Under these controlled conditions the relation between valve opening and flow rate can be determined using equations available in DIN norms (DIN Deutsches Institut für Normung e. V., 2005).

However, the pressure drop through the valve is not controlled or measured in operating conditions and the installed flow characteristic perceptibly differs from the inherent flow characteristic. The variation of the pressure in the pipe is highly dependent on the installation, especially if pipe components like valves, sensors, or elbows are present. Therefore, to obtain accurate conversion of the valve opening to utility flow a calibration procedure for each valve configuration is necessary. Two different models for flow description were selected comprising a small number of parameters to be fitted to reduce the number of measurements required for calibration. These models correct the exponential relation between mass flow and valve opening which characterizes the equal percentage valves. This correction is necessary because the pressure drop through the valve and the total pressure drop in the pipe on which the valve is installed change with the valve opening because of pipe geometry and hydraulic reasons. However, both models do not include the variation of pressure due to different heating conditions assuming a constant pressure drop across the valve for each valve opening. The influence of this assumption is discussed in more detail in Appendix D. Generally, it can be inferred that in multiproduct batch plants, where each piece of equipment is used for similar process steps (i.e., similar types of operation and operating conditions), neglecting the pressure drop may introduce an average relative error on the energy utility flow calculation between 7% and 12% depending on the valve opening (i.e., the greater impact would arise from fully open valves).

The first model is based on empirical considerations (Chan, 2007) and defines a sigmoid curve comprising two-parameters (x_1, x_2) for calibration:

$$Q = \frac{x_1 \cdot VO^2}{\sqrt{x_2 + (1 - x_2) \cdot VO^4}} \qquad 3.1$$

The second model is derived from valve characteristics (Wade, 2004) taking into account the maximal flow at full valve opening, the ratio between the maximal valve pressure drop and the total pressure drop of the flow in the pipe defined as the valve authority, and the valve rangeability. These different characteristics are expressed by three parameters (x_1, x_2, x_3) in the flow model for calibration:

$$Q = \frac{x_1}{\sqrt{1 + x_2 \cdot ({x_3}^{2(1-VO)} - 1)}} \qquad 3.2$$

After establishing a list of all valves existing in the chemical batch plant, there are two ways to proceed with the calibration. The first is the trivial way of direct calibration for each individual valve. It is practical to use an external mobile flowmeter, that is, that does not involve cutting the pipe, which can be applied for a certain period of time to each valve, either during normal operation or partial shutdown period, where the valve opening varies or can be made to vary significantly. This type of valve calibration is an accurate but time-consuming procedure, especially when a big number of valves have to be calibrated in the plant under investigation. An extreme scenario of this category is the case where instead of using an external flowmeter the calibration of all valves is performed during a full shutdown period using the overall plant flowmeter. In this case only one valve can be varied at a given period and the response of the overall flowmeter is registered to obtain the calibration curve.

The second way is to attempt to calibrate all valves simultaneously during a long period of normal plant operation using only the existing overall plant flowmeter for every energy utility (Straehl, 2009). The concept here is to link the overall building consumption and all valve openings at a given time interval for a large number of such intervals. A multiple nonlinear regression analysis based on the method of the least-squares can be used to solve this calibration problem according to eq 3.3-3.6:

$$\min_{x_1,x_2}(Q_{Building,Meas,t} - Q_{Building,Theo,t})^2 \qquad 3.3$$

so that

$$Q_{Building,Theo,t} = \sum_{v=1}^{n} \frac{x_{1,v} \cdot VO_{v,t}^2}{\sqrt{x_{2,v} + (1 - x_{2,v}) \cdot VO_{v,t}^4}} \qquad 3.4$$

$$\overrightarrow{lb_1} < \overrightarrow{x_1} < \overrightarrow{ub_1} \qquad 3.5$$

$$\overrightarrow{lb_2} < \overrightarrow{x_2} < \overrightarrow{ub_2} \qquad 3.6$$

The values for the total consumption of the building $Q_{Building,Meas,t}$ can be typically obtained from the building flowmeter for each time interval t. $Q_{Building,Theo,t}$ can be calculated from the valve opening data according to eq 3.4. This equation consists of two terms: the aggregation of all flows defined from the valve openings using the flow model described in eq 3.1 and the time independent base consumption of the building (BC). It is also possible to use the model according to eq 3.2 or any other model that links valve opening to utility flow for the representation of the variable part of the consumption. The manipulated variables during the fitting procedure are the parameters ($x_{1,i}$,$x_{2,i}$) of the model flow for each valve and the base consumption BC. The base consumption refers to utility consumption of the building not related with production operations, like pipe losses, building heating/cooling or energy used to keep some storage tanks at a constant temperature. If an estimation of BC is available prior to multiple nonlinear regression (e.g., measured during a production shut-down period), it can be used to either set BC to a constant value or validate the regression results.

3.2.2 Step 2: Thermal losses modeling

The bottom-up modeling approach is based on the energy balance of each unit operation in the plant and has been already proposed and applied in previous studies regarding energy consumption in chemical batch plants (Bieler et al., 2004, Szijjarto et al., 2008). In summary, for each unit operation the theoretical energy demand is calculated according to eq 3.7 on the basis of mass and energy balances for a given time interval t, assuming that pseudo steady state conditions have been achieved.

$$E_{Theo,t}^{UO} = \left(m_{prod,t} \cdot \bar{c}_{p,prod} + m_{equip} \cdot c_{p,equip} + m_{H/C_{sys}} \cdot c_{p,H/C_{sys}}\right) \cdot \Delta T_{prod,t} + m_{evap,t} \cdot \Delta_{vap}H + r_t \cdot \Delta_r H \cdot \Delta t - E_{Diss,t}^{UO} + E_{Loss,t}^{UO} \qquad 3.7$$

The required data to perform the energy balance calculations can be classified into two categories: those that are typically registered in the plant documents or monitoring system (material properties, for example, mixture compositions and physical properties, equipment properties, for example, mass, heat capacity and external surface, and process data, for example, reactor temperature, weight of reaction mixture, distillate flow rate) and those that are not often available, like a detailed reaction rate expression (r_t) and an expression for the losses term ($E_{Loss,t}^{UO}$). Previous studies (Bieler et al., 2004, Szijjarto et al., 2008) assumed a homogeneous distribution of reaction enthalpy over the reaction period, which may result in unit operation modeling inaccuracies, especially when energy consumption peaks are present. In the present study a kinetic formulation for reaction enthalpy is used to assess its influence on energy utility consumption. The kinetic formulation can be fitted using measured energy consumption profiles as inferred by the corresponding valve openings. To not fit thermal loss and kinetic model parameters simultaneously, the thermal loss model parameters for an equipment–utility pair should be first fitted for unit operations not involving reactions.

Using the real utility consumption ($E_{Util,t}^{UO}$) determined by the valve opening (step 1) and comparing this measurement with the result of the theoretical energy calculation it is possible to evaluate the thermal losses. A model previously developed for steam consumption (eq 3.8) in chemical reactors has been extended in the present study to more utilities and equipment (Szijjarto, 2008).

$$E_{Loss,t}^{UO} = E_{Util,t}^{UO} - E_{Theo,t}^{UO} = a \cdot (E_{Theo,t}^{UO})^b \pm k \cdot A \cdot (T_{prod,t} - T_{amb}) \cdot \Delta t \qquad 3.8$$

The parameters a, b, and k for the thermal losses model are assumed to be only equipment dependent for a given type of utility and therefore constant over time for any given process taking place in the specific equipment. These parameters can be fitted using nonlinear regression as described in previous studies (Szijjarto, 2008). The sign for the second term in eq 3.8 describing thermal losses due to radiation and free convection from the equipment surface is positive for heating and negative for cooling operations.

It is important to note that the efficiency calculated on the basis of thermal losses does not directly refer to deviations of batch execution procedures compared to “standard batch procedures”, for example, because of approximate tuning or malfunctions of the control valves. If, for instance, temperature control implies alternated use of heating and cooling utilities, the presented methodology for estimating the energy utility consumptions is still valid using a sufficiently narrow time-window for data acquisition. But in this case, the calculated theoretical consumptions for heating and cooling utilities would not directly depict this inefficient use of energy through the calculated thermal losses, but only through comparison to similar unit operations in the same or other plant equipments. This implies, that if a sufficient number of batches and equipments is monitored in a multipurpose batch plant using this approach, the derived average performance and batch-to-batch variability estimates may be used to define critical unit operations for subsequent optimization efforts.

3.2.3 Step 3: Bottom-up approach

The validation of the modeling performance can be performed from unit operation to production line level (i.e., a series of unit operations involved in the production of a chemical product), but it will be based on formerly calibrated valve openings, since there are typically no energy utility flowmeters dedicated for this lower level of aggregation. On the other hand, validation can also be performed at plant level by aggregating all model based utility consumptions and comparing this sum with the plant overall utility consumption, for which a flowmeter is typically available. The utility quantities are derived by dividing the model based energy consumption by the vaporization enthalpy in the case of steam or by the heat capacity multiplied with the temperature difference of the utility flow for brine and water. A crucial point for a robust validation at plant level is to identify and include in the aggregation all energy consumption relevant unit operation tasks. However, it is possible that some unit operation tasks lack necessary process data to complete the model based estimation of the energy consumption. If these unit operations are left out, the validation of the model based energy consumption part at plant level is not possible. Therefore, to consider the utility consumption of these unit operations the flow based on the calibrated valve openings should be used. Obviously, an energy efficiency analysis on the basis of thermal losses is not possible for these unit operations.

3.3 Case study plant description

The methodology presented above was carried out in two batch production buildings of an agrochemical company in Switzerland. In the first building, two products are manufactured using the same equipments on a single product campaign mode. The second building is a multiproduct building comprising four production lines (i.e., series of equipments) each one dedicated to only one product. Among these four chemicals, three are produced batchwise and the last one is a continuous regeneration of a common reactant used in the case study building as well as in other buildings of the plant. Every production campaign is performed without interruption. Shutdown periods are organized only for maintenance purposes or to adapt the production line to new campaigns. Every equipment is assigned to its own specific production step. Most of the equipments are standard reactors with nominal volumes between 6.5 and 12 m^3. Additional filters and dryers are also available. The batch size is constant for all processes and fixed to the maximum productivity of each production line.

Both buildings are supplied with cooling water extracted from a nearby river, 5 bar steam and brine composed of calcium chloride 30%w/w solution at a temperature around −28 °C. The second building has a third cooling medium composed of water and ethylene glycol 50% w/w at a temperature of −1 °C. This utility is continuously cooled with brine through different heat exchangers. A hot water distribution system is mainly used for heating the infrastructure (i.e., keeping the building and pipes at a desired temperature) and is fed by steam condensates. A schematic representation of the case study plant is presented in Figure 3-1.

All valves in both buildings are equal percentage valves and most of the control equipment was installed in the 1990s with only few direct flowmeters, mainly for the continuously operated distillation columns. Direct valve calibration was performed with the help of an external ultrasonic flowmeter (Optisonic 6300, Krohne). The advantage of this device is the possibility to measure without interfering with the production processes, that is, the flowmeter was installed near a valve and the measurement was taken during operation. However, this device can measure only liquid flow and therefore was used only for water and brine measurements.

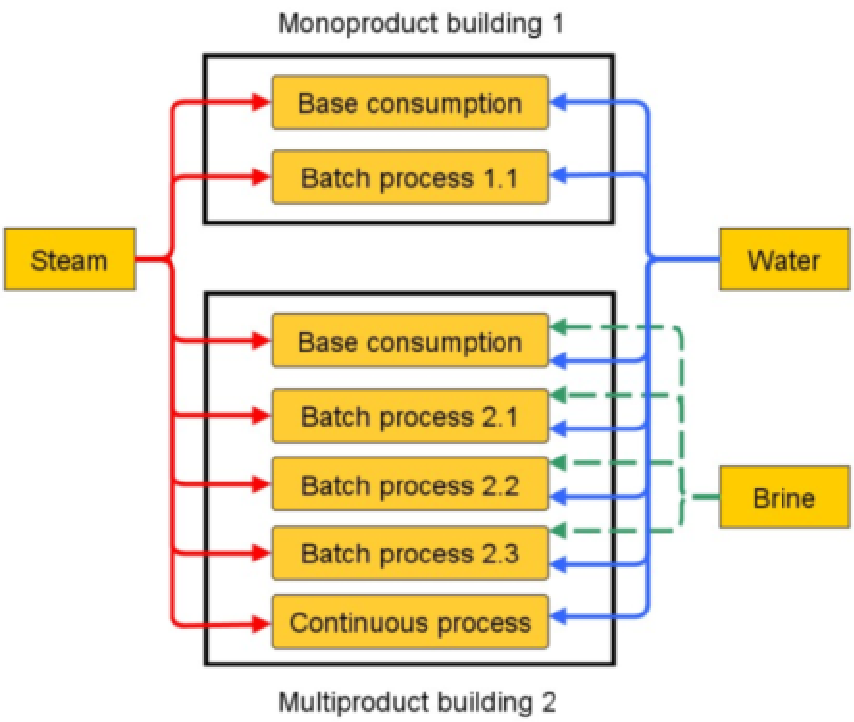

Figure 3-1 : Overview of the case study plant composed of one monoproduct and one multiproduct building. Batch process 1.1 refers to one production line producing two different products in a single campaign mode and batch processes 2.1–2.3 refer to production lines dedicated to three different products. Steam, water, and brine are the main energy utilities in both buildings.

In the monoproduct building steam control valves were calibrated using the general flowmeter of the building during a shutdown period. Each valve was calibrated using a set of different valve openings (stepwise calibration). In the multiproduct building no shutdown period was planned for all processes at the same time. To overcome this problem the method of indirect calibration was applied based on multiple nonlinear regression. For the regression of the calibration parameters the total steam consumption recorded by the building flowmeter and the valve openings of all steam control valves were used. The measurement campaign involved data collection on 1-min basis during one week. Similarly, all model based energy consumption calculations were also performed on 1-min basis and used measurements of dynamic process data recorded by the IT system of the batch plant together with static data from risk assessment files and process step procedures. Generally, no “simultaneous” heating/cooling periods were observed during process operations, indicating accurate controller tuning and avoiding temperature correction with alternated use of heating/cooling utilities.

3.4 Results and discussion

3.4.1 Step 1: Utility consumption at unit operation level

3.4.1.1 Steam consumption

In this study, multiple nonlinear regression was applied for steam valve calibration. The main reason was that direct calibrations could not be performed because of external flowmeter limitations. The regression was performed as described in section 3.2.1 and the model defined by eq 3.1 was used to represent the steam flow as function of the valve opening. The first reason for this choice was a data conversion problem for valve characteristics that help to fix the range of the fitting parameters for flow models. All valve characteristics are given for water as defined by the ISO norm (DIN Deutsches Institut für Normung e. V., 2005) and correction for steam depends on information that was not available like the valve pressure drop. However, using eq 3.1 and assuming that x_1 represents the flow at full opening (Wade, 2004) it is possible to fix a narrow range for x_1 and let a broader range only for x_2. The second reason for the selection of this flow model is its greater simplicity that allows reduction of the computation time and decreases the influence of initial values for the fitted parameters.

Before the fitting procedure a preprocessing step was necessary regarding the time lag between the signal of the valve openings and the overall steam flow measurement of the building flowmeter. The reason for this correction is the difference of the reference time between the general IT system controlling the valve openings and the data logger used to record the overall consumption of the building. A rough detection of the time lag was possible by summing all valve openings and comparing the result with the overall steam flow. The value of the time lag was determined by shifting one of the time series by one time interval until the correlation coefficient between the two time series was maximized. The best correlation coefficient was found for a time lag of 3 min. The second preprocessing step was the elimination of irrelevant peaks for the overall steam flow compared to valve openings. For peaks with a value above 4000 kg/h a comparison with every valve opening was performed and if the peak did not correspond to a variation in at least one valve opening, it was assumed that there was a measurement error and the peak was removed. Through this analysis around 1% of the 11400 available data points was eliminated.

The multiple nonlinear regression analysis was performed in two steps. First, a training procedure using one part of the data was implemented to fit the calibration parameters according to eq 3.3–3.6 and then the calibrated models were validated using the rest of the measurements. This procedure was repeated for seven different training sets. Each training set comprised 5000 data points selected in a way that all valves were open at least for 50 min. The results of this procedure are presented in Table 3-I, where the correlation coefficient R^2 was used to select the most appropriate fitting having as criterion the best validation performance. The best fitting set has an R^2 of 0.754 and a difference of 4.7% with the value obtained during the training step, indicating no significant overfitting.

Table 3-I : Calibration performance for steam control valves in the multiproduct building using various training and validation data sets[a]

data set	R^2 for training data set	R^2 for validation data set	R^2 decrease [%]
1	0.836	0.638	23.7
2	0.824	0.705	14.5
3	0.786	0.699	11.0
4	**0.792**	**0.754**	**4.7**
5	0.764	0.670	12.3
6	0.737	0.713	3.9
7	0.766	0.560	26.9

[a]R^2 is used as measure of agreement between the aggregated steam consumption according to calibrated valve openings and the measurement obtained by the building flowmeter (11 300 total measurement points, approximately 50% of which are used in the training sets). The selected set used in the rest of the study is highlighted in bold.

Figure 3-2 compares measurements and calculated values for the overall steam flow of the multiproduct building. The calculated steam flow resulting from the aggregation of the calibrated valve openings is generally in good agreement with the building overall flowmeter, although in some cases there is a trend to underestimate the real consumption. Different factors may lead to this underestimation. First, the data logger recording steam flow at building level measures flow within a 0.3 s time interval while the recording of valve openings by the IT system has a lower time resolution (1-min time interval). The result of this effect is that the apparent changes of the valve opening are slower and with a smaller amplitude. A second factor is the larger pressure difference that occurs when a closed valve is opened. This leads to different flow conditions compared to normal operation until this pressure difference is reduced. As calibrations were performed over a long measurement time, calibration curves mainly represent conditions of small pressure difference and they do not accurately calculate the value of the flow in highly dynamic conditions which occur during-opening or closing a valve (see also Appendix D). The last factor explaining some deviations is that a small number of valves were not included in the calibration because they are not controlled by the IT system. These valves control special uses of steam like heating the hot water storage when the amount of steam condensates used for this purpose is not sufficient. To check the importance of all these deviations an average value for steam flow was calculated over a 30 min interval (Figure 3-3). The comparison between the measured and the calculated values shows that extreme deviations have disappeared and confirms the hypothesis of isolated inconsistencies in the valve calibration procedure.

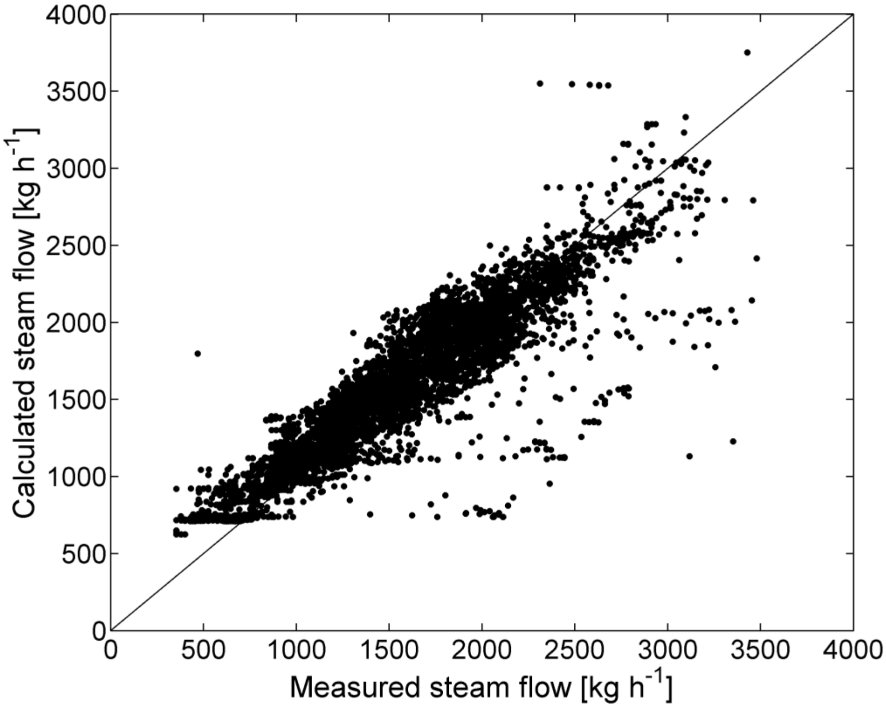

Figure 3-2 : Scatter plot of measured versus calculated flow for steam control valves calibration using a multiple nonlinear regression analysis based on 11300 measurements (1-min time interval, R^2 = 0.82).

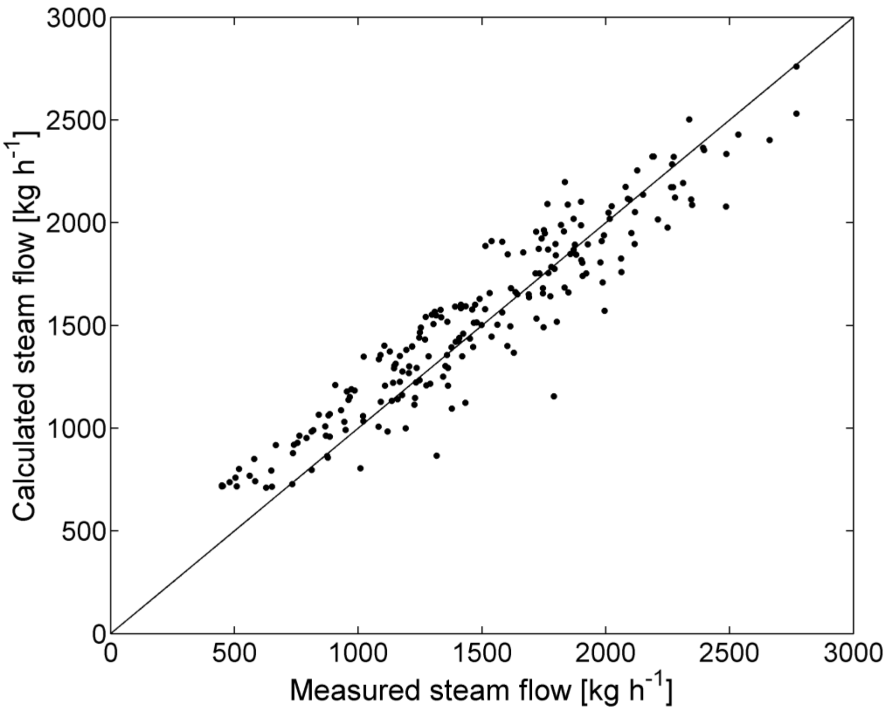

Figure 3-3 : Scatter plot of measured versus calculated flow for steam control valves calibration using a multiple nonlinear regression analysis (average values over a 30 min time interval, R^2 = 0.89).

Table 3-II : Calibration parameters of the steam control valve flow model (See eq 3.1) using multiple nonlinear regression analysis[a]

valve no.	K_{vs} (m^3/h)	DN	fitting parameter	value of x_1(kg/h), x_2	confidence interval (significance level α = 0.05)	valve type
1	8.99	50	c_1	3.93×10^{3}	4.96×10^{-3}	regulated
			c_2	7.64×10^{-1}	4.34×10^{-1}	
2	14.04	50	c_1	1.75×10^{3}	2.34×10^{-1}	regulated
			c_2	1.28×10^{0}	4.27×10^{-1}	
3	14.04	65	c_1	4.43×10^{2}	2.64×10^{1}	regulated
			c_2	4.03×10^{-3}	1.74×10^{-3}	
4	14.04	50	c_1	1.66×10^{3}	3.59×10^{2}	regulated
			c_2	1.82×10^{0}	1.03×10^{0}	
5	14.04	50	c_1	2.23×10^{3}	1.20×10^{-1}	regulated
			c_2	1.87×10^{1}	7.01×10^{0}	
6	8.99	50	c_1	1.44×10^{3}	1.72×10^{2}	regulated
			c_2	3.12×10^{0}	1.12×10^{0}	
7	8.23	40	c_1	1.83×10^{2}	3.12×10^{1}	regulated
			c_2	1.00×10^{1}	2.75×10^{-12}	
8	8.99	50	c_1	$\mathbf{8.79\times 10^{2}}$	$\mathbf{1.33\times 10^{2}}$	regulated
			c_2	$\mathbf{3.84\times 10^{0}}$	$\mathbf{3.34\times 10^{0}}$	
9	14.04	65	c_1	1.40×10^{4}	7.34×10^{-3}	regulated
			c_2	9.11×10^{0}	2.37×10^{0}	
10	3.49	25	c_1	2.07×10^{2}	3.92×10^{1}	on/off
			c_2	1.00×10^{1}	3.03×10^{-13}	
11	14.04	65	c_1	5.63×10^{3}	2.94×10^{-1}	regulated
			c_2	2.68×10^{0}	6.65×10^{-1}	
12	1.21	15	c_1	5.79×10^{1}	8.24×10^{0}	regulated
			c_2	1.00×10^{1}	0.00×10^{0}	
13	14.04	65	c_1	7.41×10^{3}	9.74×10^{-2}	on/off
			c_2	2.77×10^{0}	3.72×10^{-1}	
14	0.22	25	c_1	$\mathbf{4.89\times 10^{0}}$	$\mathbf{3.76\times 10^{2}}$	regulated
			c_2	$\mathbf{2.00\times 10^{1}}$	$\mathbf{4.58\times 10^{1}}$	
15	3.49	25	c_1	1.67×10^{2}	8.24×10^{0}	on/off
			c_2	1.00×10^{1}	0.00×10^{0}	
16	1.12	15	c_1	1.02×10^{2}	3.60×10^{1}	regulated
			c_2	1.61×10^{-1}	4.58×10^{-1}	
17	3.54	25	c_1	$\mathbf{9.14\times 10^{1}}$	$\mathbf{4.17\times 10^{2}}$	regulated
			c_2	$\mathbf{6.27\times 10^{-1}}$	$\mathbf{8.10\times 10^{0}}$	
18	1.4	25	c_1	$\mathbf{3.11\times 10^{1}}$	$\mathbf{1.58\times 10^{2}}$	on/off
			c_2	$\mathbf{2.00\times 10^{1}}$	$\mathbf{1.16\times 10^{2}}$	
19	3.49	25	c_1	3.69×10^{2}	3.66×10^{1}	regulated
			c_2	1.00×10^{1}	0.00×10^{0}	
20	14.04	65	c_1	3.49×10^{3}	7.38×10^{-3}	regulated
			c_2	1.16×10^{2}	6.83×10^{-1}	
BC				6.22×10^{2}	4.30×10^{1}	

[a]Parameters with relatively large confidence intervals are highlighted in bold.

The calibration parameters for all steam control valves are presented in Table 3-II. The confidence intervals for these parameters were determined on the basis of the covariance matrix using a significance level of 0.05. Large confidence intervals appear mainly for smaller valves with K_{vs} values below 4 m^3 h^{-1}. Smaller valves are generally employed in equipments like heat exchangers used to preheat feeding streams. There, the steam consumption is usually smaller compared to steam use in distillation or heating steps in large reactors and therefore modifications of their flow through the fitting parameters does not significantly affect the overall steam consumption (i.e., the sensitivity of the overall steam consumption to these parameters is low). However, not all valves with small K_{vs} values have large confidence intervals for their calibrated parameters and there are also some valves with higher K_{vs} values, for example, valve No. 8 with a K_{vs} of 9 m^3 h^{-1}, having large confidence interval. This is because a second factor for the appearance of large confidence intervals is the low duration of the use of the valves. For example, valve No. 8 provides steam for a regeneration step of one process and this regeneration takes place only every two or three batches when enough material is stored to start the operation.

3.4.1.2 Water and brine consumption

In the multiproduct plant, the calibration of the valves used for liquid utilities was performed with the external ultrasonic flowmeter separately for each valve during normal plant operation. During this calibration procedure two kinds of problems were detected: the measured flow was not well correlated with very fast valve openings and during most of the operations the utility consumption was kept constant at only few different levels resulting in limited measurement points and reduced calibration quality. In these cases measurements were performed in the downtime between two consecutive batch operations with valve openings covering the whole opening range. Having sufficient data points it is possible to compare different calibration models, e.g., the ones presented in eq 3.1 and 3.2 as well as an exponential model to test the nonideality of the equal percentage valve hypothesis.

The results for water and brine are presented in Figure 3-4 and Figure 3-5 respectively. The difference between measurements and the exponential equation, which is the theoretical flow representation of equal percentage valves in controlled conditions (constant pressure drop of 1 bar as defined for standardization of control valve), clearly showed other influencing factors, like pipeline and equipment related pressure drops, especially for large valve openings. The two-parameters model fitted sufficiently well the data forming a sigmoid curve (Figure 3-5) but was less successful for data points with a more exponential pattern (Figure 3-4). Figure 3-5 presents a typical example of bad valve size selection with respect to its regulatory range. The problem does not lie on the fact that a higher flow rate is required according to the process conditions, but that effective control can be done mainly in the range between 0.1 and 0.4. Moreover, both in Figure 3-4 and Figure 3-5, a disadvantage of the two-parameters model can be identified, that is, the model always passes through the origin and this is not the case for some valves, where even with a valve opening equal to zero a flow can still be detected, either due to leakage or to incorrect registration of the real valve position.

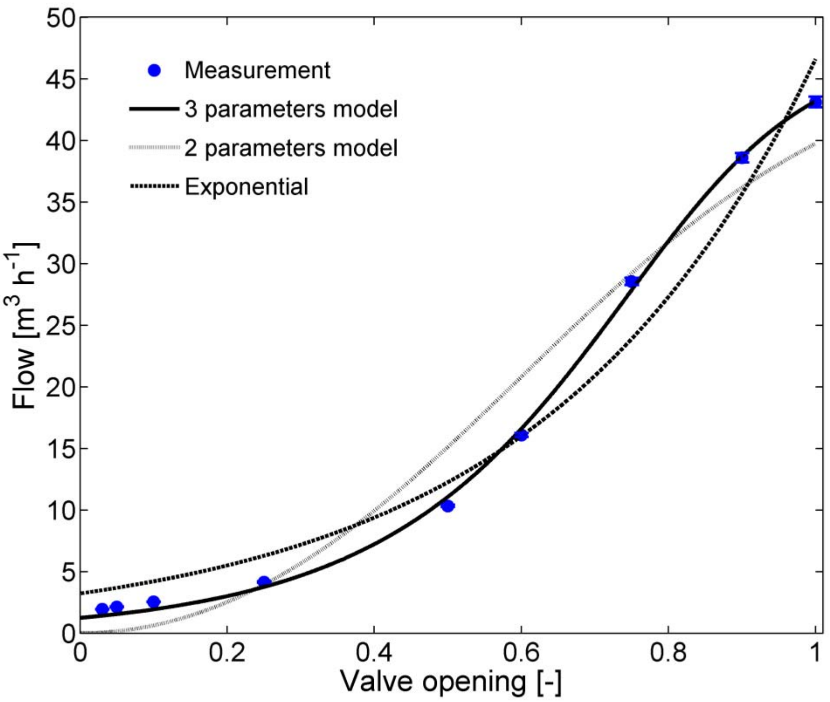

Figure 3-4 : Water control valve calibration using an external ultrasonic flowmeter and three different flow models: an exponential model corresponding to an equal percentage valve, the 2-parameters model presented in eq 3.1 and the 3-parameters model presented in eq 3.2. The measurement error of the ultrasonic flowmeter indicated by error bars lies between 1% and 3% of the measured value depending on the pipe diameter. The increased complexity of the 3-parameters model is justified by its superior adjusted R^2 value (0.999 over 0.966).

An additional fitting parameter could be integrated in eq 3.1 to model this feature, but this implies more measurements at small valve openings where data are difficult to obtain (important signal noise) to accurately fit this parameter. Moreover, the increased complexity of the three-parameters models is justified by the obtained error decrease, as this is indicated by the adjusted R^2 metric reported in Figure 3-4 and Figure 3-5. As a result, the three-parameters model, whose functional form already integrates this feature, was preferred to calibrate valves distributing liquid utilities both in the multiproduct and the monoproduct plant.

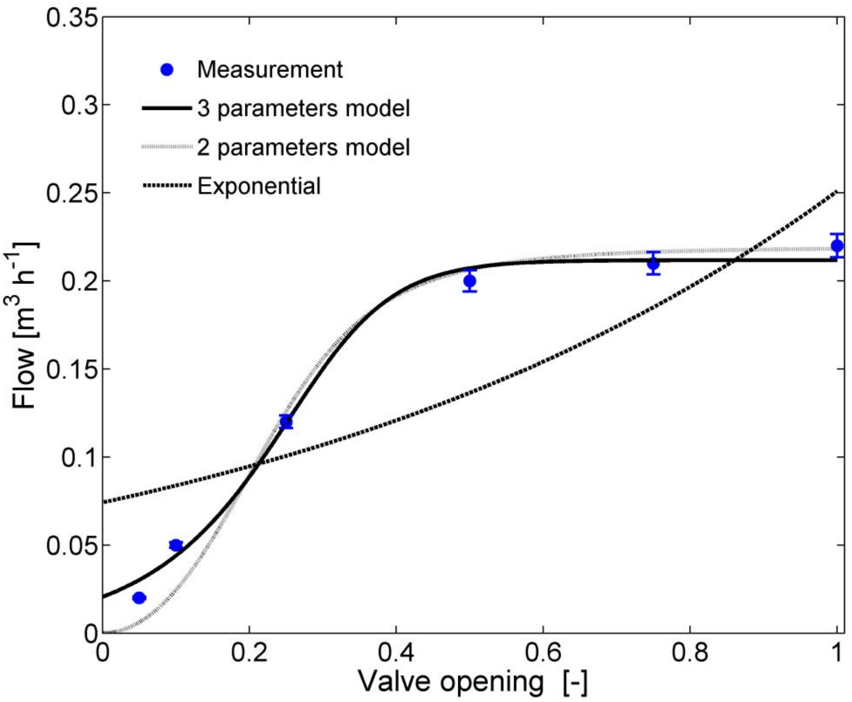

Figure 3-5 : Brine control valve calibration using an external ultrasonic flowmeter and the same flow models used in Figure 3-4. The measurement error of the ultrasonic flowmeter indicated by error bars lies between 1% and 3% of the measured value depending on the pipe diameter. The increased complexity of the 3-parameters model is justified by its superior adjusted R^2 value (0.993 over 0.974).

3.4.2 Step 2: Thermal losses modeling

Having estimated the utility consumption at unit operation level through the valve opening, the comparison between the theoretical energy demand and the real energy consumption was possible. The difference between these two quantities, defined herein as thermal losses, is used to fit the parameters of the respective loss model (eq 3.8) for different equipment–utility pairs. The results are presented in Table 3-III where the values of the fitted thermal loss model parameters are displayed along with the characteristics of the equipment and the utility type. The mean relative error between real and modeled (i.e., theoretical energy demand plus thermal losses) utility consumption on batch basis ranges between 4% and 21%

and serves as an indicator for the quality of the model at unit operation level. The respective mean relative error on 1-min basis is generally higher and ranges from 7% to 31% for most of the cases, while a few greater values (42%, 75%, and 80%) are also observed. Although this indicates that not all dynamic phenomena are captured by the thermal loss model formulation, these greater relative error values can be certainly avoided by decreasing the time resolution. Therefore, the accuracy of the predicted energy consumption for typical heating/cooling, reaction, evaporation or distillations steps, lasting from a few minutes to a few hours, is expected to vary between these two extreme cases (1-min and batch basis), the greater error values tending to disappear as the process step duration increases. The aforementioned model performance evaluation should serve as a reference basis for not varying pressure drop. As demonstrated in Appendix D, if this assumption does not hold, an additional relative error between 7 and 12% on average may be expected in the calculation of the real utility consumption. Alternatively, steam flow calculations can be based on first-principles (see Appendix E), requiring significantly more data if assumptions for thermal losses and heat transfer coefficients should be avoided and replaced by detailed calculations.

Focusing on the different utility types, it can be inferred as a general trend that water and brine consumption is less accurate than steam consumption modeling. The main reason is the conversion of the theoretical energy demand to utility amount. In the case of steam, mass flows are obtained by dividing the model derived energy demand by the vaporization enthalpy which can be easily determined. In the case of water and brine, the model derived energy demand has to be divided by the respective heat capacity and the temperature difference between input and output flows of the utility during heat exchange. As this temperature difference is not accurately measured, it increases the uncertainty of the calculation.

Table 3-III : Thermal loss model parameters fitted for various equipment–utility pairs[a]

equipment	utility	a (kJ^{-b+1})	b	K ($kW/(m^2\ K)$)	mean relative error (%) 1-min basis	mean relative error (%) batch basis	Efficiency (%)
reactor 10 m^3	water	6.93	0.61	0.074	19.4	8.6	73.5
(stainless steel)	steam	6.32	0.54	0.085	15.8	4.3	71.3
reactor 10 m^3	steam	4.59	0.56	0.053	12.4	6.8	68.8
(stainless steel)	water	8.41	0.42	0.079	18.2	9.4	71.6
	brine	6.36	0.71	0.087	8.5	12.5	55.3
reactor 10 m^3 (stainless steel)	brine	10.60	0.61	0.078	26.8	17.3	42.8
reactor 12 m^3	water	5.23	0.72	0.089	26.7	12.5	59.0
(stainless steel)	brine	7.62	0.89	0.092	7.2	9.1	45.7
reactor 10 m^3 (glass lined steel)	water	11.21	0.64	0.021	17.3	13.9	63.5
reactor 6.4 m^3 (stainless steel)	steam	4.81	0.68	0.095	31.3	9.6	64.9
reactor 8 m^3 (stainless steel)	steam	5.93	0.49	0.061	26.6	9.7	56.9
reactor 10 m^3	steam	7.70	0.79	0.090	12.5	6.7	67.2
(stainless steel)	water	9.30	0.68	0.033	16.8	9.4	58.3
reactor 10 m^3	steam	6.80	0.79	0.072	13.5	5.8	52.7
(glass lined steel)	water	2.33	9.88	0.043	19.3	12.4	56.2
reactor 10 m^3 (stainless steel)	water	7.23	0.53	0.051	16.3	15.6	61.3
reactor 10 m^3	steam	9.25	0.55	0.041	20.1	6.7	64.3
(stainless steel)	water	2.33	0.68	0.033	28.3	20.2	58.2
reactor 10 m^3	steam	15.95	0.60	0.010	20.0	5.2	53.9
(stainless steel)	water	9.56	0.70	0.002	22.1	13.4	62.6
condenser 27 m^2 (stainless steel, S&T)	water	-	-	2.029 [b]	42.1	21.2	48.6
condenser 22.5 m^2 (stainless steel, SP)	brine	2.32	0.69	0.120	25.8	18.3	50.8
condenser 43 m^2 (stainless steel, ST)	water	-	-	1.967 [b]	23.5	16.7	55.6
condenser 22.5 m^2 (stainless steel, S&T)	water	-	-	2.695 [b]	27.3	16.2	40.3
condenser 27.5 m^2 (stainless steel, S&T)	water	3.12	0.87	0.059	16.4	18.5	43.7
heat exchanger 4 m^2 (stainless steel, ST)	water	-	-	3.326 [b]	13.5	18.4	38.9
water–steam mixer (steam 6 bar)	steam	-	-	0.681 [b]	17.7	4.4	48.2
rotary dryer 4 m^3 (stainless steel)	steam	3.53	0.35	0.002	80.3	4.0	54.9
reactor 40 m^3 (stainless steel)	steam	48.3	0.52	1.7e-4	-	4.4	25-70
reactor 25 m^3 (stainless steel)	steam	34.5	0.53	4.4e-4	-	18.1	25-70
reactor 25 m^3 (stainless steel)	steam	34.5	0.64	5.2e-4	-	7.7	25-70
reactor 40 m3 (stainless steel)	steam	9.95	0.49	2.2e-4	-	6.6	25-70

[a]The mean relative error between the amount of utility calculated by the models (eqs 3.7 and 3.8) and the amount of utility based on control valve opening is presented as measure for model performance on 1-minute and on batch basis. Values given at the lower part of the table (four last reactors) are those presented by Szijjarto et al. (2008). Efficiency values are also calculated as the ratio of theoretical to overall energy consumption. (S&T, shell and tube; ST, spiral tube; SP, spiral plate; P, plate).
[b]Heat exchangers do not comprise a heating/cooling system and therefore fitting parameters a and b were not determined (see also Appendix C).

Parameters for thermal losses calculated in similar studies (Szijjarto et al., 2008) are presented in the lower part of Table 3-III. Parameter b lies clearly in the same range, while parameter a has generally smaller values. Considering that the reactor sizes are different between the two studies, and therefore so is the size of the H/C systems, it can be inferred that parameter a is sensitive to this equipment characteristic. Moreover, in both studies the first part of the thermal loss model, expressed by parameters a and b and representing losses in the H/C system, accounts for the major part of the losses. Therefore, although parameter k has a different order of magnitude, its impact on the loss term is quite small and the overall energy consumption model performance is not sensitive when fitting this thermal loss model parameter.

The efficiency of energy use for every equipment–utility pair is also presented in Table 3-III and ranges between 39% and 74%. No specific difference can be detected between the efficiency when using cooling water or steam. However, in the case of brine the efficiency is marginally lower remaining always below 56%.

Finally, another interesting result of energy consumption modeling at unit operation level refers to reactions presenting important deviations from the hypothesis of homogeneous distribution of reaction enthalpy over the whole time interval. These deviations are presented in Figure 3-6a where the theoretical energy demand assuming a homogeneous distribution of reaction enthalpy over time lies above the energy delivered by steam during the first heating step and below during the second one. This asymmetry indicates that the deviation from the assumption of homogeneous reaction enthalpy distribution is significant and kinetics should be taken into account. Since no kinetic data were available, a first-order reaction was assumed and fitting of the kinetic expression parameters was performed using reaction enthalpy and reactant mass provided by safety analysis sheets and process data, respectively. The results are presented in Figure 3-6b where a significant improvement in modeling accuracy can be observed. The thermal loss model parameters (a, b, k) of this reactor were defined prior to kinetic fitting in a unit operation not involving reaction, since they are assumed to be independent of the unit operation type for a given equipment–utility pair.

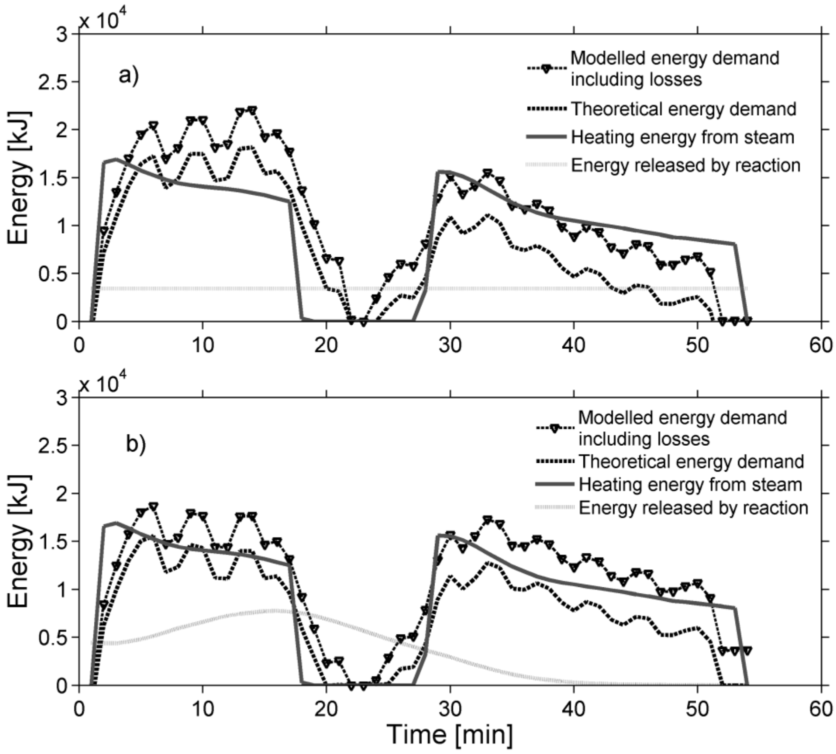

Figure 3-6 : Influence of kinetics of an exothermic reaction on the calculation of the theoretical energy demand: (a) homogeneous distribution of reaction enthalpy over time and (b) fitting of first-order reaction kinetics. Two heating steps are carried out to start and complete the reaction.

3.4.3 Step 3: Bottom–up approach

A detailed analysis of one production line is used to demonstrate the application of bottom-up modeling for different types of energy utilities. The most energy intensive and complicated production line of the multiproduct building was selected for this analysis (production line 1 in Figure 3-1). Using around 60 batches the average utility consumption and the standard deviation was calculated for each production step according to valve openings. In Figure 3-7 and Figure 3-8 this indirect measurement is compared with the model estimation for steam and cooling water consumption respectively. The agreement for both average values and variability lies within the accuracy limits claimed for unit operation modeling on batch basis (relative error between 4% and 21%, as mentioned in section 3.4.2), especially for the important, more energy intensive production steps (step 4 for steam (Figure 3-7), and steps 1 and 7 for cooling water (Figure 3-8)). Moreover, considering that a different calibration method was used for steam and water the similarity of the results indicates that both methods perform satisfactorily.

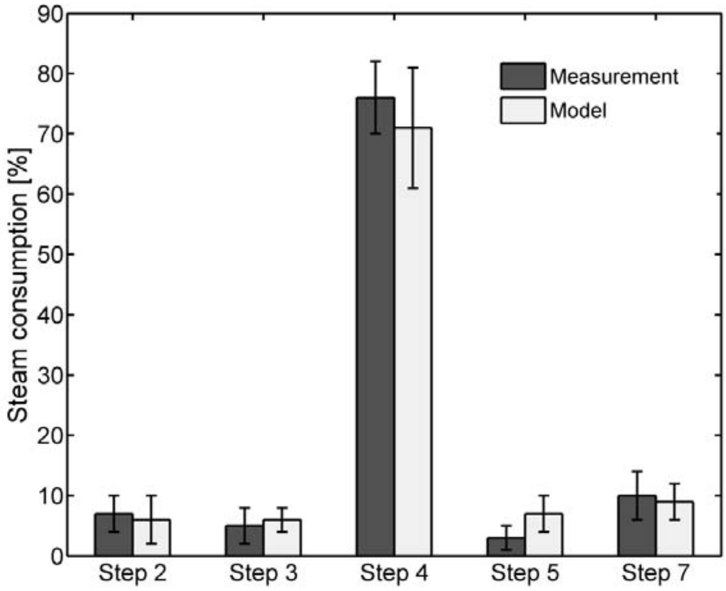

Figure 3-7 : Comparison of the average steam consumption per batch for production line-1 in the multiproduct building (see Table 3-IV) as measured based on indirect control valve calibration and estimated by the bottom-up model. The values are given in relative terms using as reference basis the total energy consumption of the batch. Error bars represent the batch-to-batch variability of the steam consumption during the model validation period. Steam is not used in the steps not presented in the graph.

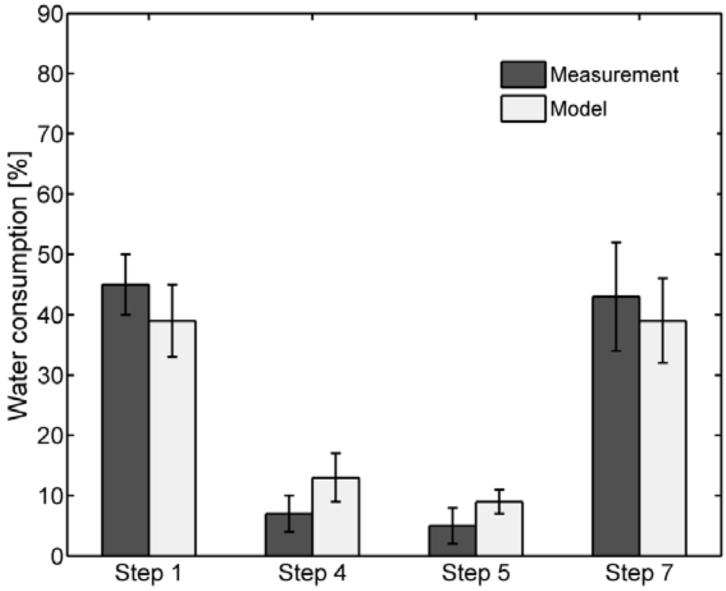

Figure 3-8 : Comparison of the average cooling water consumption per batch for production line-1 in the multiproduct building (see Table 3-IV) as measured based on direct control valve calibration and estimated by the bottom-up model. The values are given in relative terms using as reference basis the total energy consumption of the batch. Error bars represent the batch-to-batch variability of the cooling water consumption during the model validation period. Cooling water is not used in the steps not presented in the graph.

Table 3-IV : Energy utility consumption and complexity of batch production lines in the multiproduct building[a]

Production lines	Steam	Water	Brine	number of production steps	quantity of equipment
1	1	1	1	10	7
2	0.55	0.66	0.82	3	2
3	0.75	0.82	1.22	5	4

[a]The energy utility consumption is presented in relative terms using as reference basis the most complicated production line (production line 1), characterized by more production steps and equipments.

Further validation of the bottom-up model was performed at building level. Measurements were collected at different time intervals during a period of two months. Figure 3-9 shows the consumption of steam for the multiproduct building as measured by the building flowmeter and modeled using the bottom-up approach. Figure 3-10 and Figure 3-11 present the same kind of validation for cooling water and brine respectively. The base consumption is also presented and accounts for approximately 10–25% of the overall consumption depending on the type of utility. In the case of the multiproduct building no full shutdown periods were available to determine the base consumption of steam, water and brine. The base consumption for steam is estimated by the multiple nonlinear regression for the calibration of the valves. For water, the same percentage calculated in the monoproduct building during production shutdown in winter was assumed. For brine, time periods were found where only few continuous unit operations were consuming this utility. Since for continuous unit operations utility measurements were available, the base consumption for brine was calculated from the difference of these measurements and the overall consumption according to the building flowmeter. This was done for three different periods and an average value was taken.

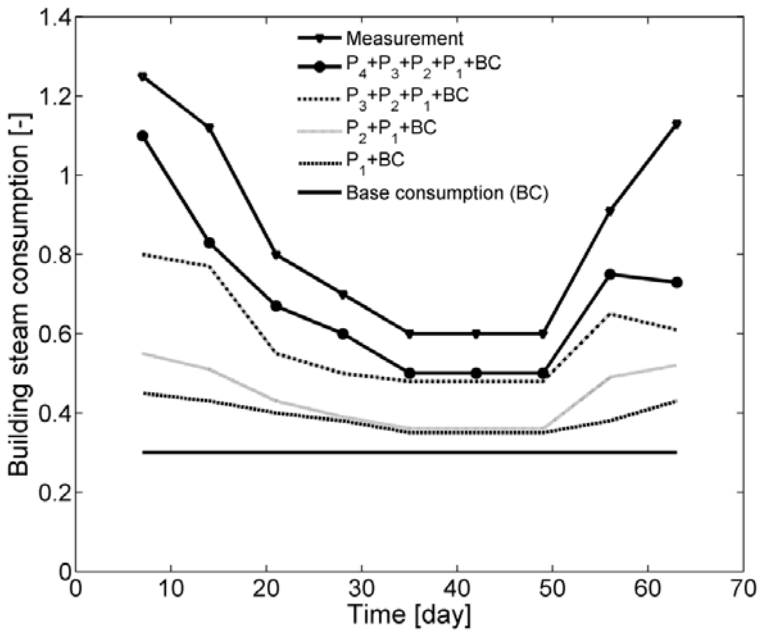

Figure 3-9 : Bottom-up modeling for steam consumption in the multiproduct building on weekly basis. The values are given in relative terms using as reference basis the average building consumption over the 1-week period used for steam control valves calibration (see Figure 3-2 and Figure 3-3). The measurement curve is obtained from the plant flowmeter. The values for processes P1–P3 refer to model results for batch processes (2.1–2.3 in Figure 3-1), while the values for P4 refer to plant measurements for the continuous process in the multiproduct building. The base consumption is estimated by multiple nonlinear regression for steam control valves calibration. The average relative modeling error at building level is 22%.

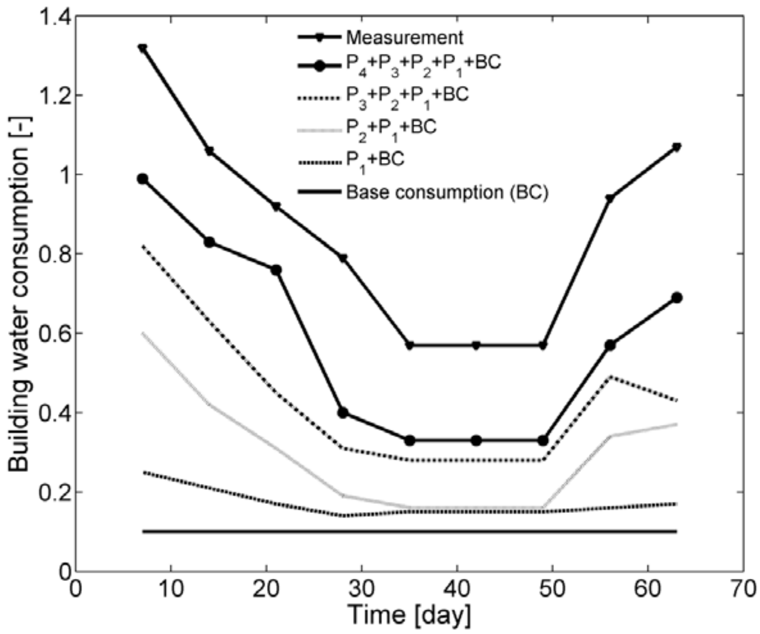

Figure 3-10 : Bottom-up modeling for cooling water consumption in the multiproduct building on weekly basis. The values are given in relative terms using as reference basis the average building consumption over 1-week period of normal operation. The measurement curve is obtained from the plant flowmeter. The values for processes P1–P3 refer to model results for batch processes (2.1–2.3 in Figure 3-1), while the values for P4 refer to plant measurements for the continuous process in the multiproduct building. The base consumption is estimated using the same ratio of base consumption to overall consumption measured in the monoproduct building during production shutdown in winter. The average relative modeling error at building level is 32%.

In all cases (Figure 3-9, Figure 3-10 and Figure 3-11) the bottom-up model estimation for utility consumption is smaller than the measured consumption of the building. The reason for this unaccounted utility consumption are operations related to maintenance, like storage tank cleaning or pipe heating for material transfers, which are not described in the batch process step procedures and also not recorded by local utility flowmeters. Furthermore, some operations during production are performed in manual mode and are not registered in the IT system. These additional operations result from equipment failures or deviations from the process specifications and are not accurately defined to be incorporated in the bottom-up model. Nevertheless, even with this unaccounted utility consumption, the mean relative error for all type of utilities ranges from 22 to 35%, values that are in agreement with those reported in previous studies (Bieler et al., 2004, Szijjarto et al., 2008). The same trends are depicted in Figure 3-12, where the daily steam consumption of the multiproduct building is compared to the results of the bottom-up model for a time period subsequent to the one used for valve calibration with multiple nonlinear regression.

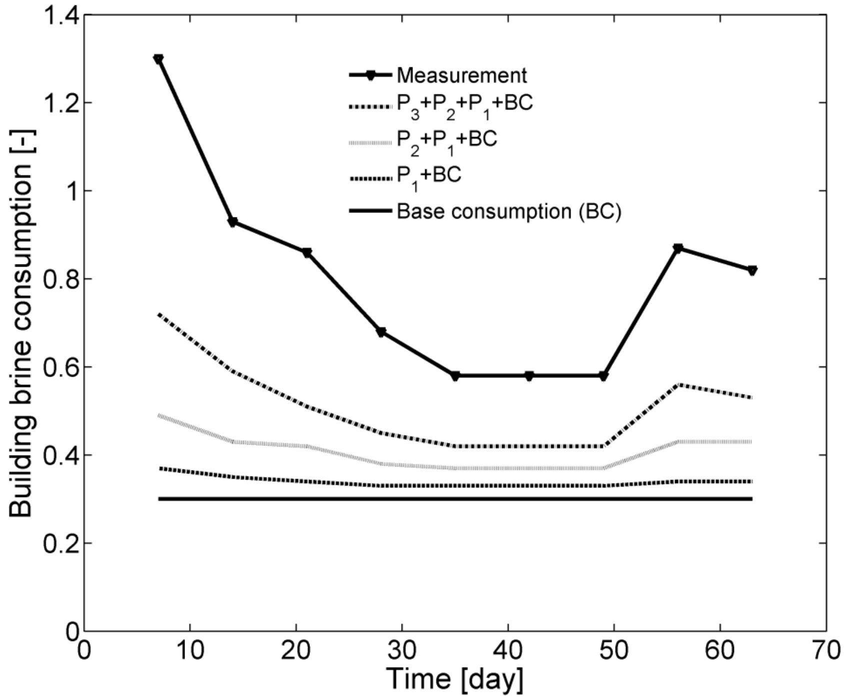

Figure 3-11 : Bottom-up modeling for brine consumption in the multiproduct building on weekly basis. The values are given in relative terms using as reference basis the average building consumption over 1-week period of normal operation. The measurement curve is obtained from the plant flowmeter. The values for processes P1–P3 refer to model results for batch processes (2.1–2.3 in Figure 3-1). The base consumption is estimated during partial production shutdown periods in the multiproduct building where brine was only used in the continuous process. The average relative modeling error at building level is 35%.

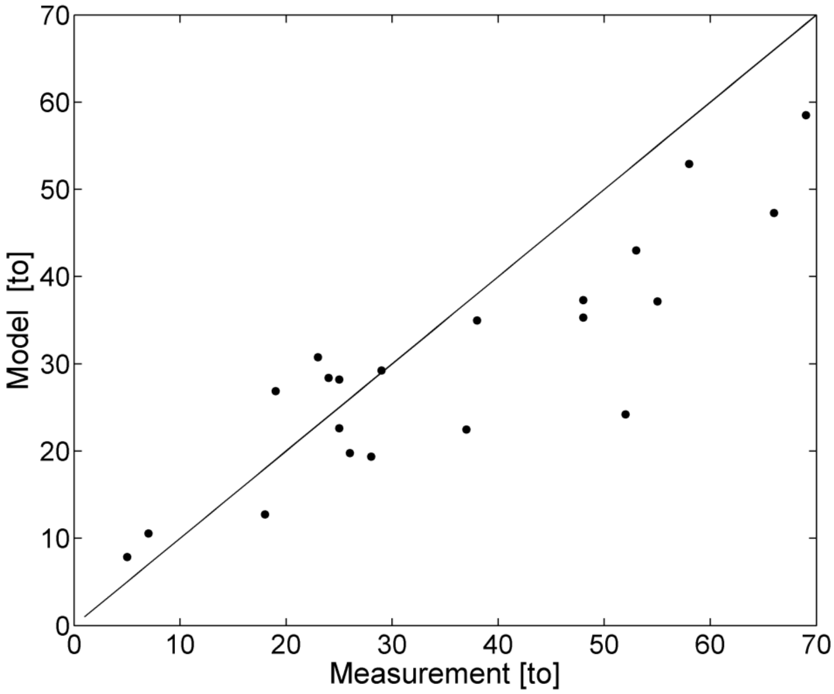

Figure 3-12 : Series of daily measurements for steam consumption in the multiproduct building compared to bottom-up model results. The average relative modeling error at building level is 21%.

Another observation from the comparison of Figure 3-9, Figure 3-10 and Figure 3-11 is that the deviations between bottom-up model and measurements for liquid utilities are bigger than those for steam. This is partially due to uncertainties in modeling batch process cooling operations and partially due to uncertainties regarding measurements of auxiliary cooling operations. As already pointed out during modeling at unit operation level, one reason is the conversion of energy utility flows resulting from modeling to utility mass with an uncertain temperature change. Furthermore, as cooling water is very cheap, its consumption is not very well controlled especially for smaller flows like condensation in vacuum pumps or motor cooling. The distribution of cooling water was often controlled by on/off valves and measurement of those flows was not possible due to small pipe size or complex pipe network preventing the use of external flowmeters. In these cases values were taken from equipment design information involving a large degree of uncertainty. The respective cooling water consumptions are generally small but exist in all main equipment (reactor, filter, and dryer) and contribute not only during the use of the vacuum pump but during the whole use of the equipment connected to the vacuum pump.

Modeling of brine consumption (Figure 3-11) was less accurate than modeling of cooling water consumption due to operation mode and calibration reasons. As brine is mainly used for postcondensation its consumption is strongly dynamic in short time intervals where valve opening changes very fast and the conversion of energy to mass flow becomes less accurate due to delay in temperature change compared to flow change. In addition, brine is distributed in a pipe network with small diameters where the liquid has a turbulent flow even for small throughput. This influences the quality of the calibration using the external flowmeter which is optimal for laminar flow and becomes less accurate for turbulent flow. Moreover, the high temperature change implies an important variation of the physical properties of brine (e.g., density, viscosity, etc.), while the flowmeter provides a mass flow from sound speed measurement using constant properties at a reference temperature.

A similar bottom-up modeling analysis for the case of the monoproduct building is provided in the Appendix A. The modeling error at plant level is naturally reduced for all energy utilities consumption because of the lower degree of plant complexity. Moreover, a top-down approach for one process of the monoproduct building is also presented (Appendix B, Figure 8-5) demonstrating that even in this simpler case there is difficulty to estimate energy utility consumption based purely on productivity data.

3.5 Conclusions

A systematic procedure was developed to analyze the energy utility consumption at unit operation level in batch chemical industry. Different methods were tested to determine the real utility consumption based on the opening of control valves. Knowing the real utility consumptions allowed an estimation of the thermal losses by comparison to the theoretical energy demand calculated using recipe description and process data. Parameters of thermal loss models were fitted for various equipments-energy utility pairs performing diverse unit operations. The developed models for steam, water and brine consumption were validated at unit operation, production line and building level, with relative error ranging from 4 to 35% depending on the type of utility and aggregation level. This level of accuracy verifies the extension of the bottom-up modeling approach to more types of equipments and utilities compared to previous studies. It also provides plant managers and process engineers with reference values for efficiency of energy use for most of the standard equipments and utilities used in batch chemical industry.

Furthermore, the concept of the bottom-up approach can be advantageous in everyday industrial practice compared to the traditional daily or weekly reading of utility consumption based on building flowmeters, because it offers the possibility to backtrack the sources of the deviations in the sublevels of the bottom-up modeling when uncommon consumptions are detected. For instance, the production step level analysis allows the identification of unit operation tasks consuming large amount of utilities. This screening procedure is necessary for any optimization efforts in plants comprising many equipments and lacking direct flowmeter measurements, which is a typical case even in nowadays multipurpose chemical batch plants. Moreover, even though some newer industrial facilities are equipped with various measuring devices at equipment level, a significant number of existing facilities is expected to operate in the coming decades and plant retrofitting priorities in batch plants are, even nowadays, typically not energy related. For this reason, model-based estimation of real energy flows remains a valuable tool for plant monitoring and optimization. Finally, the determination of equipment–utility specific parameters describing thermal losses can offer a new criterion for unit operation-equipment selection in process design and scheduling.

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Chapter 4

4 Integrated waste management in batch chemical industry based on multi-objective optimization

4.1 Introduction

Elimination of waste generation and treatment of hazardous wastes are important environmental challenges of chemical industry in order to fulfil legal emission limits and comply with sustainability targets. The importance of this challenge was already depicted in the “Green Chemistry” methodology (Anastas and Warner, 1998), where the first principle is the prevention of the waste generation, and received some attention in the engineering field with the development of the “Green Engineering” concept (Garcia-Serna et al., 2007). In general, the integration of the waste problem in the development of chemical processes is relatively recent (Cano-Ruiz and McRae, 1998), including, for example, methodologies like the “Waste Reduction” (WAR) algorithm (Hilaly and Sikdar, 1994, Hilaly and Sikdar, 1995), the synthesis of mass-exchange networks (El-Halwagi and Manousiouthakis, 1989), and expert systems like ENVOP (Halim and Srinivasan, 2002). However, despite the clear benefits of these waste minimization approaches in process design, waste generation is often not negligible. Thus, end-of-pipe technologies are still needed and waste treatment design efforts typically focus on low treatment costs and environmental impacts at least below the respective legislation limits.

In this direction, Roberge and Baetz (1994) described a waste treatment system of a petrochemical plant with the help of mathematical modeling, analyzed the effect of waste reduction on the treatment operations, and performed an economical optimization over a period of 25 years. A similar model was developed by Alidi (1996), including recycling operations besides treatment and disposal. A weighted multi-objective optimization approach on the basis of theoretical data and an analytic hierarchical process was also presented. Hogland and Stenis (2000) introduced an analysis based on Life Cycle Assessment (LCA), including economic and energy objectives. Their method presented the implementation of a new waste management system for an industrial site and compared the base case to the energy optimization alternative and the material recovery optimization alternative. Chakraborty and Linninger (2002) described an overall system for chemical waste treatment to define the most appropriate operations according to economic and environmental objectives using combinatorial optimization. Simplified operation models were built to calculate utility consumptions and emissions as a linear function of the waste stream compositions or flows. This superstructure aimed to support long-term operation (Chakraborty et al., 2003) and investment planning under uncertainty conditions while satisfying emission limits (Chakraborty and Linninger, 2003). In a similar approach, Cavin et al. (2001) presented a tool to optimize industrial waste treatment, including a sequence of optional and terminal operations and using cost and ecological scarcity as environmental assessment indicators. This system also handles uncertainty in waste composition and in treatment efficiency.

It should also be noted that the use of LCA for development of sustainable waste management was introduced by (Barton et al., 1996), who described the Life Cycle Inventory (LCI) and the appropriate way to model unit operations for flowsheeting of waste management systems. The authors provided a detailed list of treatment operations and their influence on waste characteristics. This led to the development of several models for municipal waste LCA tools (Morrissey and Browne, 2004), and comparative studies have also been performed to quantitatively analyze their results (Winkler and Bilitewski, 2007) and identify the differences in the model assumptions (Gentil et al., 2010).

On the other hand, only limited work has been done on the operating conditions of industrial waste management systems to improve their efficiency. A traditional approach is the optimization of operating conditions for existing waste treatment facilities according to multiple objectives. This procedure is well known for the design and the operation of chemical processes (Azapagic, 1999) and can be applied straightforwardly to waste management systems. For example, Ramzan et al. (2008) studied the optimization of recovering waste solvents by distillation where the steam consumption and the reflux ratio are used as variables to find optimal conditions for a set of environmental indicators.

Another approach is the mixing of waste streams to achieve improvements in existing facilities. Experimental studies of waste mixing in sewage sludge for anaerobic digestion were performed in order to optimize the biogas generation (Rao and Baral, 2011). Liu et al. (2011) studied the environmental impact of mixing municipal sludge and oily industrial wastes with coal for constant steam generation in an industrial plant. The emissions and utilities consumption of several mixing scenarios were analyzed, indicating that a partial replacement of coal with sludge reduced the total impact of the utility generation. Cavin et al. (2006) further developed their initial system by including stream mixing in multi-objective optimization. Moreover, LCA models for municipal units have been used for final treatments, allowing a more accurate inventory of emissions into the environment.

Another approach is the modification of waste treatment scheduling to further increase the degrees of freedom in operating conditions. Yundt et al. (1994) optimized the operations scheduling for a batch waste management system focusing on makespan improvement. Intermediate storage was considered along with different equipment configurations and heuristics. Duque et al. (2009) performed multi-objective optimization using environmental indicators for the design and scheduling of a recovery network for specific industrial wastes. Their work focused on the transportation of wastes and selection of optimal sites for treatment using a “State-Task-Network” representation.

This study focuses on an industrial waste management system of a chemical batch plant in Switzerland. The models for the waste treatment units are taken from previous LCA studies based on industrial data (Capello et al., 2005, Koehler et al., 2006, Seyler et al., 2005). They are integrated into a mathematical framework for operating cost calculation and environmental impact assessment. The framework includes operating constraints according to actual industrial procedures and a check of legal compliance for the emissions to the environment. Multi-objective optimization is performed to investigate the more cost effective and environmentally benign ways to simultaneously treat a given set of waste streams. Trade-offs are identified based on Pareto front calculations. Different sets of waste streams are analyzed in different operating conditions, and a multiperiod formulation introducing the influence of production planning on the waste mixing problem is also studied.

The rest of the paper is structured in the following way. First, the model of the waste management system is described and the optimization framework including all constraints is given in detail. Then two industrial case studies are introduced involving different sets of waste streams and operating conditions. The first case study (CS1) refers to a small set of continuously produced waste streams and, besides incineration, wet air oxidation, and wastewater treatment plant, two different model configurations for solvent recovery through distillation are tested. The second case study (CS2) includes the same waste treatment options but handles a larger number of waste streams produced in batch mode and analyzes the influence of waste availability as function of production planning. Next, the optimization results are presented and the influence of waste mixing solutions on both objective functions (i.e., operating costs and Eco-indicator 99) is thoroughly discussed. Finally, the main conclusions are summarized and interesting research directions for future studies are identified.

4.2 Methods

4.2.1 Description of the structure of the waste management system

The structure of the liquid waste treatment system is defined to resemble the typical industrial system under investigation and to facilitate economic and environmental analysis according to scenarios involving different sets of waste streams and operating conditions. Figure 4-1 shows this overall structure with the available treatment processes and the main material and energy flows crossing the boundaries of the system. The system comprises three types of waste treatment, that is, incineration (INC), biological wastewater treatment plant (WWTP), and wet air oxidation (WAO), as well as recycling options including batch and continuous distillation (DIST). In order to obtain an exhaustive inventory of material and energy streams, models for waste treatment operations are based on previous life cycle impact assessment (LCIA) studies: wastewater treatment and wet air oxidation processes have been studied by Koehler (2006), incineration processes by Seyler et al. (2005), and distillation processes by Capello et al. (2005). All models are mainly based on industrial data and provide emissions and utility consumptions as linear function of waste composition.

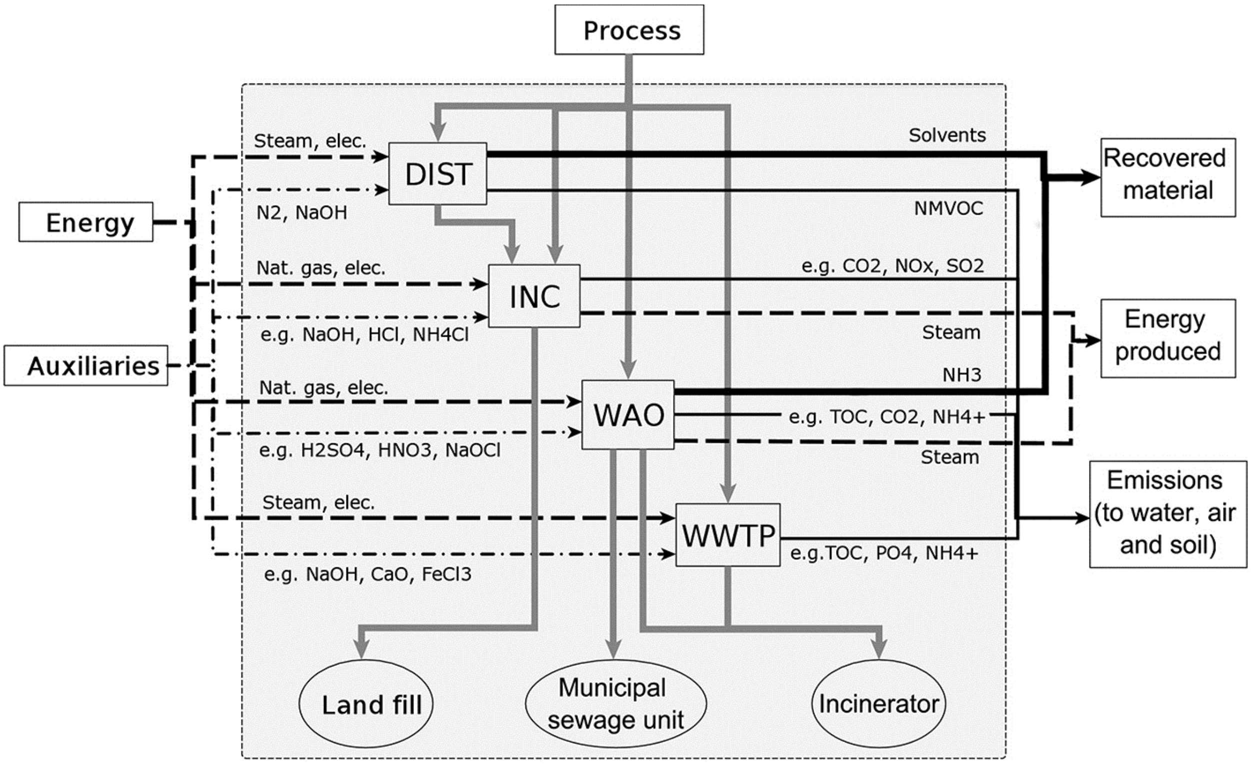

Figure 4-1 : General overview of the waste management system structure and its boundaries (dashed box). Vertical lines indicate primary waste flows and residues from the waste treatment units and horizontal lines indicate energy utilities, auxiliaries, recovered materials, and emissions flows (DIST: distillation, INC: incineration, WAO: wet air oxidation, WWTP: wastewater treatment plant).

For every type of emission and utility listed in the LCIA models, a corresponding emission and utility is selected in the Ecoinvent database (Ecoinvent Centre, 2010, Frischknecht and Rebitzer, 2005). If a utility is not defined in the Ecoinvent database, the generic organic or inorganic chemical is used in order to estimate the respective environmental impact. Table 8-IV, Table 8-V and Table 8-VI in Appendix G provide all data used in the economic and environmental impact calculation.

It should be noted that for some output streams of the LCIA models the impact of the final disposal is not described by the linear correlations, and therefore has to be added for a complete evaluation of the environmental impact. The impact of these final disposal processes is again calculated according to data available in the Ecoinvent database. More specifically:

- In the presence of metallic catalysts in the input waste stream of INC, metal precipitation in the washing water used to clean the flue gas of incineration has to be performed. The residual material containing heavy metals is disposed in specific landfill, that is, similar to the sludge from wastewater treatment of steel rolling also containing heavy metals.

- For the liquid output of WAO containing traces of total organic carbon (TOC) above the legal emission threshold, a WWTP of class-1 according to the Ecoinvent database classification is used corresponding to the treatment of streams with low TOC content.
- For the sludge resulting from the copper catalyst separation of WAO, a hazardous waste incineration plant is used, while the sludge produced in WWTP is treated in a municipal waste incineration plant.
- The impact of residue transport between treatment and final disposal sites is not considered but the electricity used for pumping waste streams to treatment units is taken into account.

In the case of distillation, Capello et al. (2005) provide relations between waste input and utility consumption in the form of statistical distributions. In the present study, the average values of these distributions are used by default, that is, neglecting the dependence on the chemical composition of waste streams. The solvent recovery is defined as a percentage of the amount of the waste solvent (80% in the case of the batch distillation and 90% for continuous distillation) after test runs of distillation scenarios using the Ecosolvent tool (Capello et al., 2008). Finally, for a better representation of the industrial system, operation limits for each treatment process and legal threshold values for emissions to air and water (Swiss Government, 1985, 1998) are imposed as constraints. A detailed description of these constraints is provided in the next section.

4.2.2 Description of the mathematical formulation of the waste management system

The optimization is performed in order to obtain (or approximate) the Pareto front for two objective functions according to eq 4.1-4.7. The first objective function (OF_1) represents the operating cost and the second (OF_2) is the Eco-indicator 99 (Goedkoop and Spriensma, 2001) used as indicator for the environmental impact. Eco-indicator 99 is a damage-oriented method for life-cycle impact assessment, a method that integrates human health, ecosystem quality, and resources utilization and uses a weighting scheme to obtain a single total score.

Among the different weighting schemes that have been proposed, the average hierarchist weighting scheme (Eco-indicator 99(H/A)) is used here, which corresponds to an equal weighting for human health and ecosystem damages (both 40% of the final value).
The cost is calculated according to the two terms of eq 4.6: The first term is proportional to the total mass or volumetric flow rate fed to the treatment unit and the second term describes the consumption of utilities for a specific pollutant in the treatment unit. From the different types of treatment, some valuable output streams are recovered and deducted from the operating cost. These include steam from INC (the electricity production described by Seyler et al. (2005) is not included in this study to keep a similar configuration with the real plant), steam and ammonia from WAO, and recycled solvents from DIST.
The environmental impact considers pollutant emissions (in air, water, and soil) and resources consumption for the waste treatment processes as defined by the LCIA models and data from Ecoinvent database (see eq 4.7). Similarly to the cost calculation, by-products of waste treatment are considered as benefit, that is, the environmental impact is reduced by the impact associated with the production of the same amount of recycled solvents or utilities. The environmental impact of the process generating the waste streams lies outside the boundaries of the overall environmental balance as depicted in Figure 4-1.
For each type of treatment, the input flow rate has to satisfy a constraint reflecting the capacity limits of the treatment unit (eq 4.2). Moreover, no waste storage is considered (eq 4.3) and each type of treatment has input limitations regarding the concentrations of waste stream components, which are linear or nonlinear functions of the flow rates, as in eq 4.4 and eq 4.5, respectively. All treatment-specific constraints are further discussed in the following paragraphs.

$$\min_{q_{i,k}} f(OF_1, OF_2) \quad s.t. \tag{4.1}$$

$$Q_{k,min} \leq \sum_i q_{i,k} \leq Q_{k,max} \tag{4.2}$$

$$\sum_k q_{i,k} = \bar{q}_i \tag{4.3}$$

$$\sum_i q_{i,k} \cdot c_{i,j} \leq \left(\sum_i q_{i,k}\right) \cdot \overline{c_{\iota,k}} \tag{4.4}$$

$$lb_{l,k} \leq g_l(q_{i,k}, c_{i,j}) \leq ub_{l,k} \qquad 4.5$$

with

$$OF_1 = \sum_k \left(cf_k \cdot \sum_i q_{i,k} + \sum_m cf_m \cdot QU_{k,m}\left(q_{i,k}, c_{i,j}\right) \right) \qquad 4.6$$

$$OF_2 = \sum_k \left(\sum_n ef_{k,n} \cdot QE_{k,n}\left(q_{i,k}, c_{i,j}\right) + \sum_m ef_m \cdot QU_{k,m}\left(q_{i,k}, c_{i,j}\right) \right) \qquad 4.7$$

4.2.3 Incineration (INC)

For the incineration, the following three operating constraints have to be considered:

$$3000 \leq \sum_i q_{i,INC} \leq 4500 \quad [kg/hr] \qquad 4.8$$

$$975 \leq \frac{\sum_i q_{i,INC} \cdot \Delta_c H_i}{Q_{fluegas} \cdot c_{p,fluegas}} \leq 1075 \quad [°C] \qquad 4.9$$

$$Q_{fluegas} \leq 18800 \quad [kg/hr] \qquad 4.10$$

The input waste flow rate is constrained (i.e., eq 4.8 derived from eq 4.2) in order to get good spraying conditions of the liquid waste in the combustion chamber for a minimum steady flow of air (lower bound) and for capacity reasons (upper bound). The adiabatic temperature rise of the flue gas is also constrained (i.e., eq 4.5 takes the form of eq 4.9 with an input temperature of 25°C for the waste flow) to ensure an efficient combustion (lower bound) and because of the maximal thermal resistance of the burner wall material (upper bound). If the available waste streams violate this upper bound of the adiabatic temperature rise, an amount of fresh water is added to decrease the flue gas temperature. This amount of water is also considered for all constraints and cost calculations.

For the calculation of the adiabatic temperature rise, the flow rate of the flue gas is calculated according to the combustion reaction: for each waste stream the theoretical amount of oxygen needed is defined according to the waste composition, then the corresponding mass of air is calculated including an oxygen excess of 9% (vol/vol), and the flue gas flow rate can be determined by adding the mass flow rate of the waste streams to the mass flow rate of air. The heat capacity is calculated proportionally to the mass fraction of each component and is a function of the temperature. An iterative procedure is used to determine at the same time the adiabatic temperature rise and the corresponding heat capacity of the flue gas.

Finally, the third constraint refers to the maximal flow rate of the flue gas (i.e., eq 4.10 derived from eq 4.5), in order to have a reaction time long enough for a complete combustion.

4.2.4 Wet air oxidation (WAO)

The following ten operating constraints are considered for the wet air oxidation:

$$5000 \leq \sum_i q_{i,INC} \leq 8200 \quad [kg/hr] \tag{4.11}$$

$$\sum_i q_{i,WAO} \cdot c_{i,j} \leq \left(\sum_i q_{i,WAO}\right) \cdot \bar{c}_{j,WAO} \tag{4.12}$$

The input waste flow rate is constrained (i.e., eq 4.11 derived from eq 4.2) for plant-specific installation design and capacity reasons. Moreover, the WAO treatment requires a specific composition to ensure a high efficiency and to protect the reactor from corrosion, as the reaction occurs at high pressure and high temperature under oxidative conditions. Nine constraints corresponding to limiting concentrations for critical components (TOC, salt, total amounts of chlorine and bromine, fluorine, iodine, total amount of phosphorus, calcium, and magnesium) have to be satisfied (i.e., eq 4.12 derived from eq 4.4). Data about these limiting concentrations are available in Table 8-VII of Appendix H. If some of the concentrations exceed the maximal values, an amount of water can be added to the waste flow rate in order to respect these constraints. This amount of water is also considered for all other constraints and cost calculations.

4.2.5 Wastewater treatment plant (WWTP)

The WWTP has to satisfy a large number of constraints regarding the degradation capacity of biomass. These are summarized as:

$$0 \leq \sum_{i} q_{i,WWTP} \leq 650 \quad [m^3/hr] \tag{4.13}$$

$$\sum_{i} q_{i,WWTP} \cdot c_{i,j} \leq \left(\sum_{i} q_{i,WWTP}\right) \cdot \bar{c}_{j,WWTP} \tag{4.14}$$

$$\sum_{i} q_{i,WWTP} \cdot c_{i,j} \leq 0.1 \cdot \sum_{i} q_{i,WWTP} \cdot \bar{c}_{j,EC50} \tag{4.15}$$

$$\frac{\sum_i q_{i,WWTP} \cdot c_{i,BOD}}{\sum_i q_{i,WWTP} \cdot c_{i,TOC}} \geq 1.5 \tag{4.16}$$

The input flow rate is constrained (i.e., eq 4.13 derived from eq 4.2) for capacity reasons (upper bound), while no minimal flow is required because if no waste is treated in WWTP, a flow of methanol is used to feed the biomass. Moreover, six concentrations have to be smaller than a maximal value (TOC, salt, sulfate, phosphate, total phosphorus, total nitrogen) according to eq 4.14 derived from eq 4.4. Data about these limiting concentrations are available in Table 8-VII of Appendix H. Additional constraints for the biological treatment arise from the sensitivity of bacteria to toxic components (i.e., eq 4.15 derived from eq 4.4). To integrate these limitations, the maximal concentration of each organic component is defined as one-tenth of the half maximal inhibitory concentration for bacteria (EC50) to guarantee no reduction in the bacteria activity. As few data of EC50 for bacteria of sewage treatment are available, values of half maximal inhibitory concentration for the marine bacteria Vibrio fischeri are used (Table 8-VIII of Appendix H). Finally, the BOD/TOC ratio has to be greater than 1.5 to ensure good biomass degradation (i.e., eq 4.16 derived from eq 4.5). If some of the concentrations exceed the maximal values, an amount of water is added to the waste flow rate in order to satisfy these constraints. This amount of water is also considered for all other constraints and cost calculations.

In the model of the WWTP, some values for pollutant reduction are modified compared to the original values given by Koehler (2006); that is, TOC and BOD removals are quite low and are not comparable with data from the studied sewage treatment. A comparison with other data sets collected from a large sample of municipal and industrial sewage treatments in Switzerland (Bernard and Mange, 2009) confirms this difference. As TOC is an important parameter of WWTP and is also part of the legal constraints, the TOC and BOD reduction efficiencies of the studied industrial plant are used in the model (TOC reduction efficiency: 0.920; BOD reduction efficiency: 0.989).

4.2.6 Distillation (DIST)

For batch distillation, a constant capacity is defined as average value according to the analysis of several batch distillation operations in production plant distillation units of 10 m^3 (eq 4.17).

$$q_{i,DIST} = 275 \quad [kg/hr] \qquad 4.17$$

The same value is used for continuous distillation. No mixing of waste streams is allowed prior to distillation. Candidate streams for distillation are selected based on their composition; that is, a stream can be sent to distillation only if one of its components has a mass fraction over 0.4 for batch distillation and 0.3 for continuous distillation. In the case of batch distillation, two solvents can be recovered, if each of them has a mass fraction greater than 0.4.

4.2.7 Legal emissions

Every solution of the optimization algorithm satisfying the operating constraints of the previous paragraphs has to comply with pollutant emission limits in air and water imposed by Swiss legislation (Swiss Government, 1985, 1998). For emissions of pollutants in water, the legislation imposes constraints for the concentrations of heavy metals (Cu, Cr), TOC, total phosphorus, ammonium, and absorbable organic halogen, while for emissions of pollutants in air the concentrations of heavy metals (Zn, Cu, Ni, Co), SO2, NOx as NO2, NMVOC, CO, particles, ammonia, HCl, HBr, and HF have to be checked. For the incineration emissions, the concentration of pollutants has to be calculated according to the air needed for the waste combustion and the combustion of the natural gas used to reduce the NOx emission, both with an oxygen excess of 9 % (vol/vol).

Two case studies are presented to target the potential for improvement by following full mixing policies compared to the limited one currently used in the investigated industrial waste management system. According to this limited mixing policy, each waste, depending on its composition, is assigned to only one type of treatment, without any possibility to use it in other waste treatment units. On the other hand, the full mixing policy allows all waste streams to be split between all types of treatment.

4.3 Cases Studies

4.3.1 Case Study 1 (CS1)

In the first case study, five waste streams enter the waste management system described in Figure 4-1, which comprises two distillation columns. The characteristics of the waste streams are provided in Table 4-I. They were selected so that their flow rates and composition depict a typical situation of the industrial plant, where each one of them would be assigned to a different waste treatment process and two streams would be assigned to distillation for waste solvent recovery. A fixed flow rate has to be treated for each waste stream (see eq 4.3). No uncertainty features were introduced in this case study regarding the waste flow rates and compositions, in order to focus solely on the impact of full mixing policies and define the level of modeling detail that allows identification of critical options overlooked in restrictive mixing policies.

Table 4-I : Information about waste streams involved in all scenarios of CS1. The organic solvents are given in parentheses (EtOH: ethanol, Tol: toluene, ButAc: n-butyl acetate, MeOH: methanol, GlyOH: 1,2-ethanediol, X: pesticide, MIBK: 4-methylpentan-2-one).

	Original treatment	Flowrate [kg/h]	Composition [%]
Stream 1	WWTP	5000	Water 99.57; salts 0.1; organic 0.33 (1)
Stream 2	WAO	3600	Water 87.41; salts 3.8; organic 8.79 (3)
Stream 3	Inc	1050	Water 3.0; salts 0; organic 97.0 (2)
Stream 4	Batch distillation	275	Water 1.0; salts 0; organic 99.0 (3)
Stream 5	Batch distillation	275	Water 0; salts 0; organic 100.0 (3)

Three different optimization scenarios are performed according to the full mixing policy: The first one includes two batch distillation columns (scenario 1), the second uses one continuous and one batch distillation column (scenario 2), and the third one (scenario 3) considers higher utility consumptions in the distillation model in the case of azeotropic mixtures in the waste streams. A scenario including only continuous distillation columns for solvent recovery was judged to be impractical for chemical batch plants because of the reduced flexibility and the additional costs of the numerous storage tanks that would have to be installed to assure a smooth operation. All scenarios are normalized for the same operation time, which is fixed to 1 hr.

4.3.2 Case Study 2 (CS2)

Case study 2 depicts a more complex problem combining production planning with waste management, under the condition that all waste generated during one campaign must be treated during the same campaign (i.e., no storage capacity is available). The system comprises again three continuous treatment units (INC, WAO, and WWTP) and two batch distillation columns. Twelve waste streams are considered, representing the waste generation of five industrial batch processes (P1 to P5) with a fixed flow rate to treat for each waste. This flow rate is calculated as the waste amount generated by each batch divided by the respective cycle time. The characteristics of the waste streams are provided in Table 4-II.

The production planning consists of two periods, and a different combination of batch processes for each period generates a different set of waste streams to be treated. Three different combinations for production planning are evaluated in the present study: P1P2-P3P4P5, denoting that batch processes P1 and P2 are performed in the first campaign with P3, P4, and P5 in the second, and P1P3-P2P4P5 and P2P3-P1P4P5, using the same notation system. The capacity of the continuous treatment presented in the constraints of the mathematical formulation is reduced to represent the corresponding fraction of the studied batch processes (P1–P5) with respect to the total capacity used in the first case study.

$$3000 \leq \sum_i q_{i,INC} \leq 1170 \quad [kg/hr] \tag{4.18}$$

$$0 \leq \sum_i q_{i,WAO} \leq 900 \quad [kg/hr] \tag{4.19}$$

$$0 \leq \sum_i q_{i,WWTP} \leq 400 \quad [m^3/hr] \tag{4.20}$$

Table 4-II : Information about waste streams involved in all scenarios of CS2. The organic solvents are given in parentheses (EtOH: ethanol, Tol: toluene, ButAc: n-butyl acetate, MeOH: methanol, GlyOH: 1,2-ethanediol, X: pesticide, MIBK: 4-methylpentan-2-one, DMF: N,N-dimethylmethanamide, FCHO: formaldehyde, FCOOH: formic acid, FCN: formamide, PentOH: 1,2-pentanediol, ProOH: 1,2-propanediol).

	Original treatment	Flowrate [kg/h]	Process	Composition [%]
Stream 1	INC	185.0	1	Water 8.2; salts 3.1; organic 88.7 (4)
Stream 2	WWTP	224.1	1	Water 87.6; salts 12.4; organic 2.9e-3 (3)
Stream 3	INC	255.0	2	Water 0; salts 0; organic 100.0 (3)
Stream 4	WWTP	215.8	2	Water 97.5; salts 2.3; organic 0.2 (3)
Stream 5	Batch distillation	225.8	2	Water 5.0; salts 0; organic 95.0 (3)
Stream 6	WWTP	303.3	3	Water 84.1; salts 4.5; organic 11.4 (5)
Stream 7	Batch distillation	87.0	3	Water 1.0; salts 0; organic 99.0 (3)
Stream 8	INC	274.7	3	Water 49.5; salts 18.0; organic 32.5 (3)
Stream 9	WWTP	20.5	3	Water 100.0; salts 2e-3; organic 1e-3 (4)
Stream 10	WWTP	575.8	4	Water 99.5; salts 0; organic 0.5 (1)
Stream 11	Batch distillation	99.2	4	Water 0; salts 0; organic 100.0 (4)
Stream 12	WWTP	26.6	5	Water 77.0; salts 0; organic 23.0 (1)

The distillation residues are treated in the same period and are added to the waste stream that is sent to the incineration (eq 4.12). If the flow rate of a stream that can be assigned to distillation is lower than the maximal capacity of the distillation column, the stream is exclusively treated using distillation and does not participate in any other mixing. Moreover, only those streams that could be currently treated in distillation units according to the industrial guidelines are considered as possible candidates for distillation (i.e., no assumption is made for utility consumption of azeotropic mixtures).

In the case of incineration, to ensure for all periods at least one organic waste and one aqueous waste for control of the adiabatic temperature rise (eq 4.9), two additional wastes are considered as being available from other parts of the production plant: an organic waste representing spent solvents, and an aqueous waste for mother-liquors. These two external wastes are defined from the average composition of all organic solvents and mother liquors treated in the incineration unit. These external wastes are not integrated in the cost and environmental impact calculations, but are only a way to balance particular combinations of waste streams with a high percentage of organic solvents or high amount of aqueous solutions, respectively.

4.4 Results and discussion

4.4.1 Case Study 1 (CS1)

Figure 4-2 presents the results of the multi-objective optimization for scenario 1. Different groups of similar mixing solutions are identified and further described in Table 4-III. The first observation is the negative value of the environmental impact for all mixing solutions. This is due either to the recovery of solvents in the distillation units or to steam production in the incineration unit. The WAO treatment produces steam too, but the overall production is small due to internal steam consumption and the benefit is overcome by the consumption of auxiliaries and electricity.

Table 4-III : Optimization results for scenario 1 of CS1 (five waste streams S1–S5 [Table 4-I], two batch distillation columns, no consideration of azeotropes). BC indicates the base case with limited mixing policy. Each flow is classified as a percentage of the total amount of every waste stream. Five classes are defined: ○ 0%, □ < 10%, ▣ 10-50%, ■ >50%, ● 100%. Streams S4 and S5 are not shown here because they are mainly sent either to distillation or incineration. The labels indicate the groups of solutions identified in Figure 4-2 (Pareto front groups are highlighted).

Label	Stream(s) to dist	Stream1 to WWTP	Stream1 to WAO	Stream1 to Inc	Stream2 to WWTP	Stream2 to WAO	Stream2 to Inc	Stream3 to WWTP	Stream3 to WAO	Stream 3 to Inc
A	3	□	■	□	□	▣	■	□	▣	■
B	3	□	■	□	□	▣	■	□	□	■
C	4	■	▣	□	□	▣	■	□	▣	■
D	3+4	■	□	□	□	▣	▣	□	▣	■
E	3+4	□	■	▣	□	■	▣	□	▣	■
F*	3+5	▣	■	▣	□	■	▣	□	□	■
G	4+5	□	■	▣	□	▣	■	□	▣	■
H	4+5	■	▣	□	□	▣	■	□	▣	■
I	4+5	■	□	□	□	■	□	□	□	■
J*	4+5	□	■	▣	□	■	▣	□	□	■
BC	4+5	●	○	○	○	●	○	○	○	●

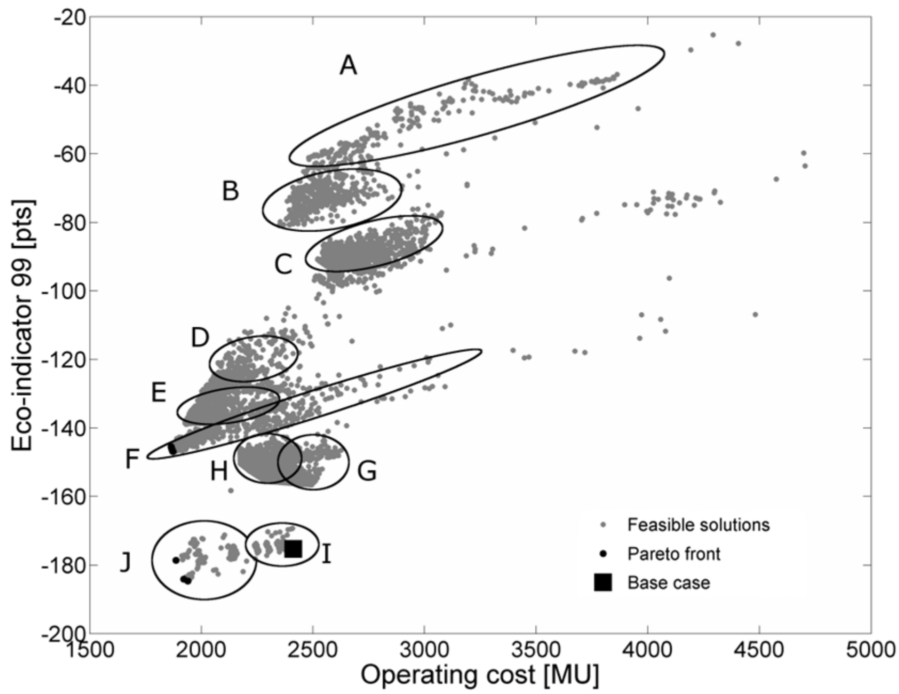

Figure 4-2 : Optimization results for scenario 1 of CS1 (five waste streams [Table 4-I], two batch distillation columns, no consideration of azeotropes). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points and the base case solution are highlighted. Groups of similar mixing solutions (A to J) are identified and their description is provided in Table 4-III.

Pareto optimal mixing solutions can be divided into two groups, J and F. Group J represents the best trade-off solution between the two objectives in the region of the lowest environmental impact and group F in the region of the lowest cost. The Pareto front is steep with respect to the environmental impact, demonstrating that the cost difference between groups J and F is marginal, both having approximately 20% lower cost compared to the base case. This is mainly achieved by a more efficient distribution of streams 2 and 3 between these units and also by using stream 1 instead of fresh water to dilute INC and WAO streams. More specifically, by adding stream 3 to the WAO feed, the TOC content increases and a better yield in steam production can be obtained. On the other hand, the amount of stream 2 sent to INC reduces the amount of salt in WAO and a lower amount of stream 1 is needed to satisfy this constraint. This leads to an overall lower feed and therefore cost for WAO. As mentioned earlier, this mixing solution allows a reduction of the fresh water compared to the base case. Fresh water is needed in the base case for dilution purposes in order to respect operating constraints. As the production of fresh water has no environmental impact, the environmental performance (Eco-indicator 99) of group J lies in the same range with the base case.

Group F has a similar pattern with group J, but recovers partially solvent from stream 3 by distillation, instead of stream 4, which is now mainly incinerated (90%) and the rest treated in WAO. This decreases marginally the treatment cost due to less overall amount treated in the INC, and additionally stream 4 causes a lower adiabatic temperature rise and, therefore, also less amount of stream 1 is now needed for controlling the temperature. Nevertheless, this benefit in the treatment cost due to the more expensive INC and WAO units is mostly compensated by the less heat recovery and the auxiliaries used in WWTP, resulting in marginal differences between groups F and J. However, this influence of the recovered energy in the environmental impact, together with the higher environmental impact for the production of the solvents in stream 4 compared to those in stream 3, favors significantly the solutions of group J in terms of the environmental objective. The aforementioned analysis is best depicted by the more detailed cost and environmental impact breakdown in Figure 4-3 and Figure 4-5, which are further analyzed for all scenarios of CS1 later in this section.

With respect to the groups of the non-Pareto optimal solutions in Figure 4-2 and Table 4-III, group I follows a mixing similar to the base case, where each waste stream is mainly sent to its predefined treatment. Groups G and H are characterized by a common pattern for handling streams 2 and 3, while their main difference lies in the treatment of stream 1. Compared to the Pareto optimal solutions of groups J and F, it can be observed that according to the pattern of groups G and H for handling streams 2 and 3 a larger amount is shifted from WAO to INC (stream 2) and from INC to WAO (stream 3). This clearly indicates the Pareto optimality in the redistribution of the waste loads with respect to the predefined treatment (base case), that is, the fact that this redistribution cannot be carried out unconditionally. Different patterns of mixing and selection of solvents to be recovered deteriorate the performance of the rest of the groups, more notably in the environmental objective, and in particular when a lower amount of solvent is recovered (groups A, B, and C). Finally, it should also be noted that the variability in the actual mixing quantities existing within the same mixing pattern also plays a role in the performance variation, ranging from Pareto (or near Pareto) optimal to clearly inferior performance (e.g., groups F and A).

Therefore, the qualitative analysis already presented is clearly accurate for the "best performance" solutions of each group, and only approximate if the average performance of each group of solutions is considered.

Similar trends can be described for scenarios 2 and 3 of CS1, the results of which are provided in detail in Appendix I (Figure 8-11 and Figure 8-12, Table 8-IX and Table 8-X). A synopsis of the optimal solutions obtained in all scenarios of CS1 is presented in Figure 4-3, Figure 4-4 and Figure 4-5.

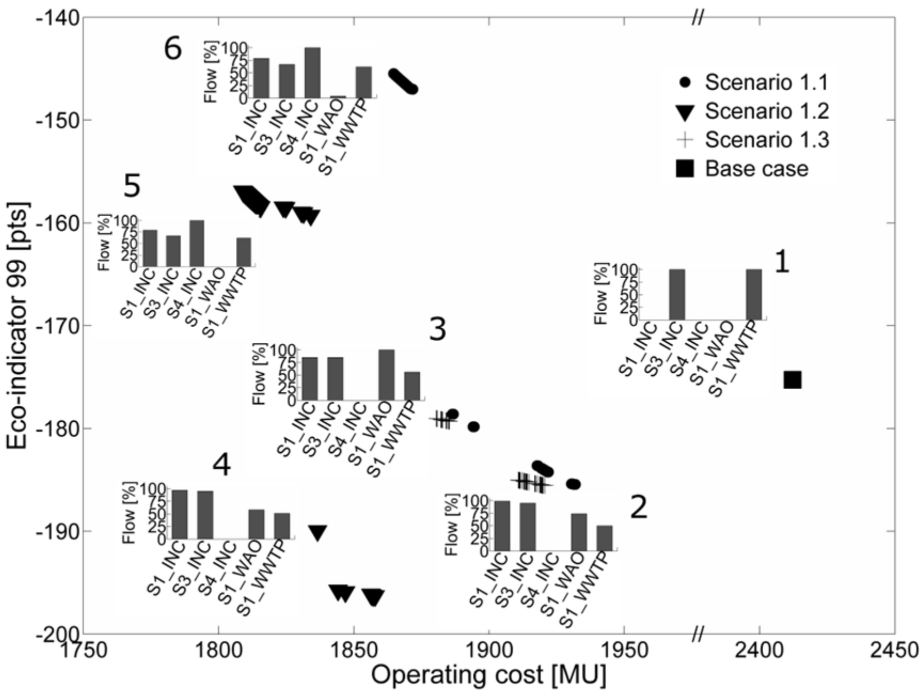

Figure 4-3 : Pareto fronts for scenarios 1 to 3 of CS1. For each scenario the anchor points of the Pareto fronts (i.e., optimal operating cost or Eco-indicator values) are described in detail with the help of bar charts (1: base case, 2: best operating cost for scenario 1, 3: best operating cost for scenario 2, 4: best operating cost for scenario 3, 5: best Eco-indicator99 for scenarios 1 and 3, 6: best Eco-indicator99 for scenario 2). The operating cost is given in arbitrary monetary units (MU).

More specifically, Figure 4-3 presents the Pareto points for each one of the three scenarios accompanied by indication of the most significant changes in the waste stream mixing profiles. In all mixing scenarios the cost performance is improved compared to the base case by 20% or higher. On the other hand, significant improvement for the environmental impact (i.e., more than 10%) is demonstrated by only a few solutions of scenario 2, where a continuous distillation column is in operation. Generally, scenario 2, at both extremes of the

Pareto front, proposes mixing solutions similar to scenario 1, and the improvement in both objectives is due to the reduced utility consumption and the higher solvent recovery of the continuous distillation column compared to batch distillation, according to the industrial-based LCIA models used in the present study. Therefore, switching completely from batch to continuous operation mode for solvent recovery may appear a reasonable choice. However, there are additional factors that should be considered, such as the higher installation cost of the equipment operating in continuous mode, the additional storage tanks for a smooth connection of the chemical batch plant with the continuous solvent recovery systems, and the reduced flexibility when there is no option for batch distillation. Scenario 3 shows a performance similar to scenario 1 regarding the best Eco-indicator 99 solutions. However, the best cost solution identified in scenario 1, by distillation of stream 3 instead of stream 4, is penalized in scenario 3 due to the higher utility consumptions assumed for azeotropic distillations and therefore does not appear as a Pareto optimal solution in Figure 4-3.

Besides the selection of recovering solvent from stream 3 instead of stream 4, another feature of the optimal cost solution profiles (not shown in Figure 4-3) is that some amount of stream 2 that was treated in WAO is now sent to INC. Stream 2 contains some amount of salts that have to be diluted, causing higher flows in WAO and increasing the treatment unit cost. However, the additional flow of stream 2 to INC contains significant nitrogen concentration generating nitrogen oxides, leading to higher emissions and therefore to higher consumption of natural gas to keep these emissions below the legal limit.

Figure 4-4 and Figure 4-5 show the cost and environmental impact decomposition of the extreme Pareto optimal solutions into the categories of auxiliaries, treatment unit and energy use. In Figure 4-4, the best cost solutions for all scenarios show a common pattern compared to the base case, that is, they have lower auxiliaries (e.g., less amount of waste treated in WWTP and WAO) and treatment unit costs (e.g., less demand of fresh water due to mixing policies leading to smaller flow rates) as well as disposal impacts (e.g., less amount of waste sent to WWTP), but they use more energy (e.g., more natural gas to control the nitrogen oxide emissions) and emit more pollutants (e.g., from combustion of higher amount of streams that also contain nitrogen). It should be noted that the environmental impact of auxiliaries is not following the respective cost reduction trend due to lower requirements in WWTP and WAO. The reason is that the solvents (ethanol and toluene) recovered from stream 3 (best cost solution) have a higher price but a lower environmental benefit compared to the solvent (butylacetate) recovered from stream 4. The comparison of the best environmental solutions in Figure 4-5 shows that the performance in all categories is improved compared to the base case (i.e., there is no trade-off compared to the base case between the different subcategories). This is due to the treatment of stream 2 in WAO and the recovery of butylacetate as explained above.

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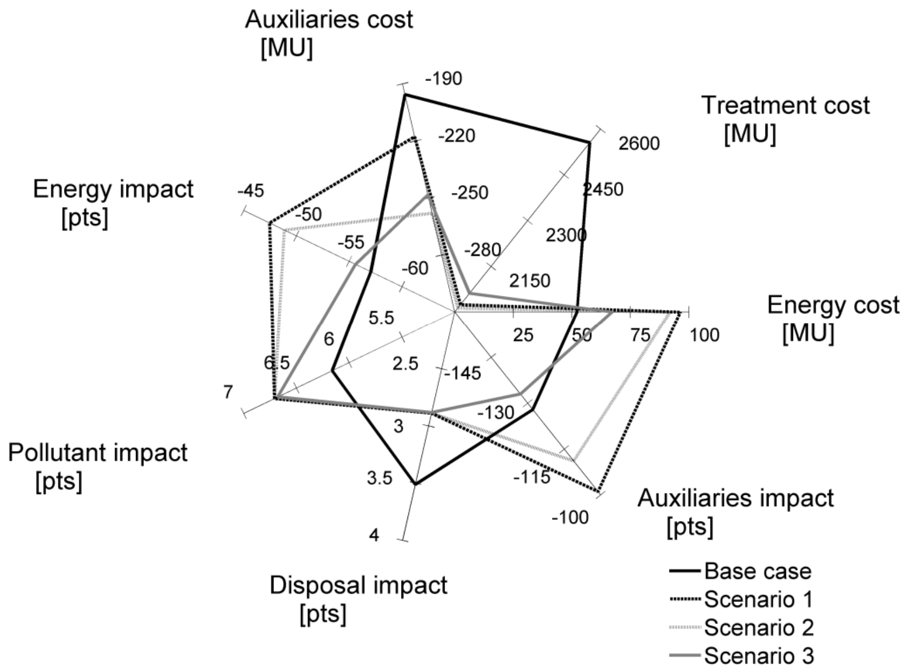

Figure 4-4 : Decomposition of operating cost and Eco-indicator values for optimal operating cost solutions for scenarios 1 to 3 of CS1. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas, steam). Pollutant impact: emissions to air, water and soil from the primary waste treatment units (DIST, INC, WAO, WWTP). Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 4-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units.

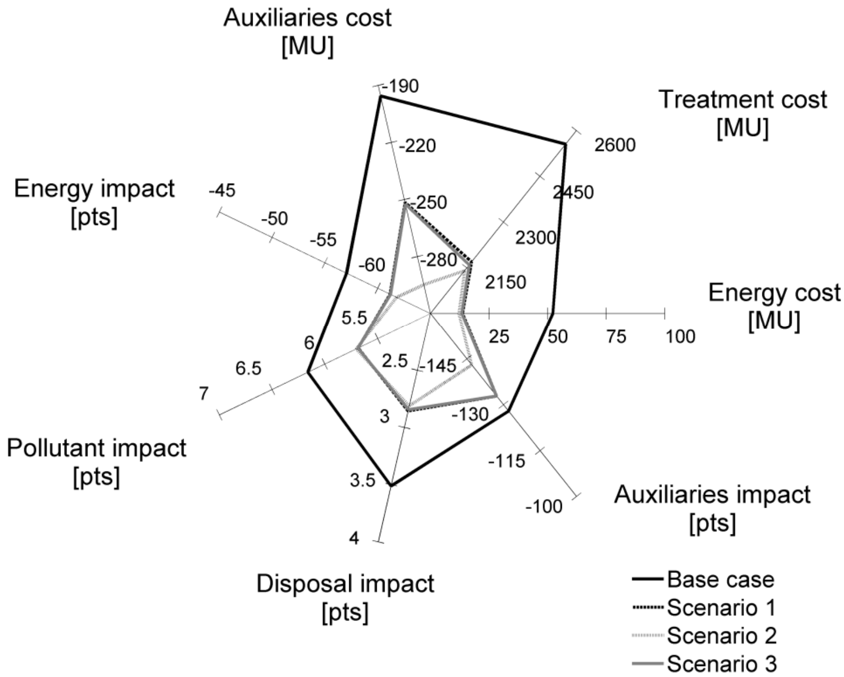

Figure 4-5 : Decomposition of operating cost and Eco-indicator values for optimal environmental solutions for scenarios 1 to 3 of CS1. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas, steam). Pollutant impact: emissions to air, water and soil from the primary waste treatment units (DIST, INC, WAO, WWTP). Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 4-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units.

A further decomposition of the auxiliary and energy cost savings and burden is presented in Figure 4-6 and Figure 4-7, respectively, for all the scenarios and solutions analyzed in Figure 4-4 and Figure 4-5. A relative comparison of the cost subcategories indicates the importance of the recovered solvents and the sodium hydroxide used in WAO for the auxiliary cost savings (Figure 4-6). The recovered solvents play also the major role for the respective environmental impact (supporting information, Figure 8-15). The steam produced by incineration and the natural gas consumption dominate the energy cost (Figure 4-7) and influence the additional energy burden compared to the base case. Electricity consumption in the thermal treatment and steam in the distillation have a smaller influence. Similar trends are observed for the environmental impact of the energy consumption (Appendix K, Figure 8-16). The cost savings with respect to the treatment units are mainly due to the decrease in the use of WAO (Appendix K, Figure 8-17). Overall, the cost savings achieved in this case study by applying the full mixing policy are equivalent to approximately 10 tons/hr of steam (i.e., approximately 20% compared to the base case) and the respective benefit for the environmental impact is equivalent to the impact of the production of 1.3 tons/hr of steam (i.e., approximately 10% compared to the base case). Extending this impact to a whole year leads to savings of approximately 2300 tons of CO2 or equivalently the impact of 500 personal cars for 1 yr (i.e., traveling a distance of 23,000 km).

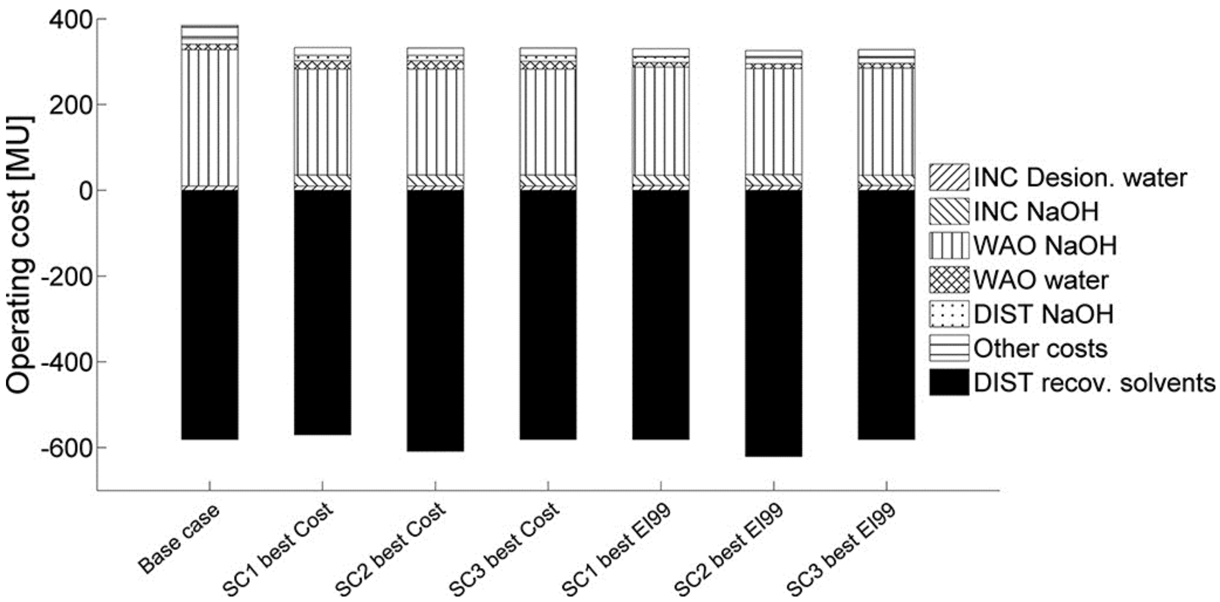

Figure 4-6 : Decomposition of the auxiliary related cost for scenarios 1 to 3 of CS1 with respect to the best cost and environmental solutions analyzed in Figure 4-5 and Figure 4-3.

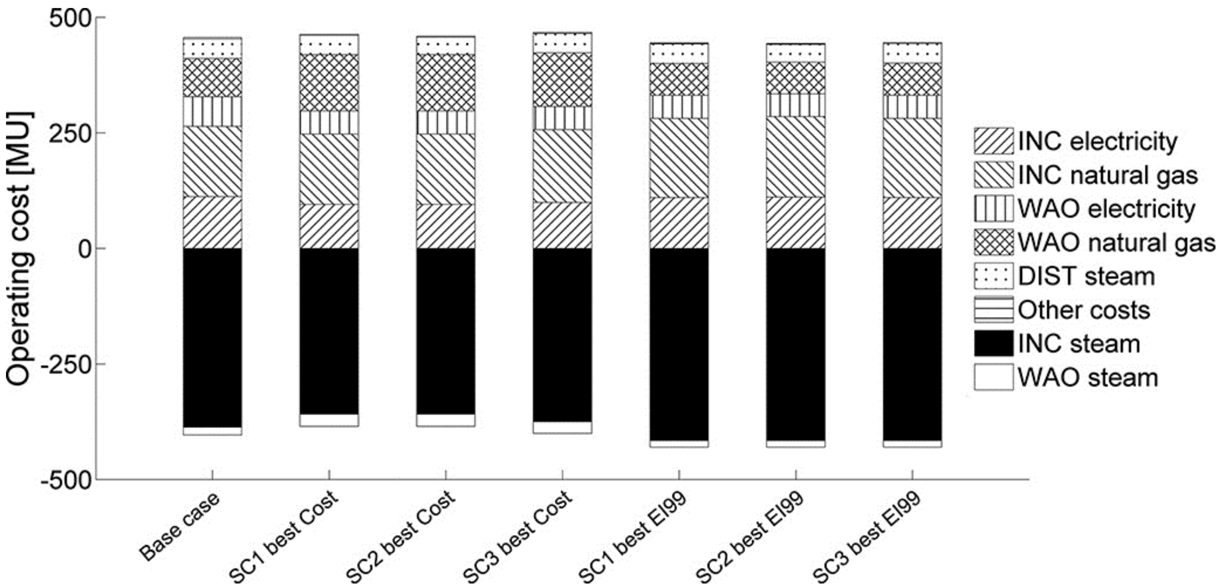

Figure 4-7 : Decomposition of the energy related cost for scenarios 1 to 3 of CS1 with respect to the best cost and environmental solutions analyzed in Figure 4-5 and Figure 4-3.

4.4.2 Case Study 2 (CS2)

In the second case study the complexity increases due to the higher number of streams and the two-period production planning. Figure 4-8 shows the optimization results for the multiperiod P1P2-P3P4P5 configuration, and the description of the solution groups is given in Table 4-IV. The base case scenario in this case study refers to limited mixing policy for the respective multiperiod planning. An improvement of more than 50% in the operating cost and more than 10% in the Eco-indicator 99 is observed for the optimal solutions compared to the base case scenario. Moreover, three groups of mixing solutions (D, E, and F) form the Pareto front. Groups D and E have similar mixing patterns regarding the percentage of the total amount of the waste treated in every treatment unit for the first period, with their difference arising from the second period, where some waste load assigned to INC in group D is assigned to WAO in group E. This also causes a redistribution of the WWTP load for diluting stream 8 of P3 in order to satisfy the TOC operating constraint of the WAO. WAO generates fewer emissions than INC but has a higher treatment cost, resulting in a marginal trade-off represented by these two groups. Group F, on the other hand, lies at the other extreme of the Pareto front (i.e., optimal Eco-indicator 99) and follows exactly the opposite pattern of group D for both periods, and the opposite pattern of group E for the first period. Compared to the base case, all Pareto front solutions improve the system performance in both objectives, mainly due to the partial transfer of WWTP loads to INC to replace fresh water for regulating the flue gas temperature. Another factor is the usage of the WAO unit, which is not part of the base case treatment policy. As mentioned earlier, this is clearly beneficial from environmental point of view, and this is more evident in the second period due to the salt content of stream 8, that is, sodium sulfate and ammonium chloride. These salts cause NOx, SO2, and HCl gas emissions in INC, while they remain in the liquid phase in WAO before finally treated in WWTP. From economic point of view, the transfer of waste loads from INC to WAO is not justified, unless capacity constraints are violated. Finally, it should be noted that the non-Pareto optimal solutions represented by groups A, B, and C do not fully exploit the incineration potential, while a different solvent recovery scenario (i.e., group A not recovering stream 11) clearly leads to deterioration in the performance of the system.

Table 4-IV : Optimization results for scenario 1 of CS2 (five products P1–P5 in two production periods P1P2-P3P4P5, 12 waste streams [Table 4-II], two batch distillation columns, no azeotropes). BC indicates the base case with limited mixing policy. Each overall flow to a specific treatment unit for a given solution is classified as larger or smaller than the median of all solutions for this specific treatment unit (reported in the table). The labels indicate the groups of solutions identified in Figure 4-8 (Pareto front groups are highlighted).

		Flow to INC		Flow to WWTP		Flow to WAO	
Label	Streams to DIST	Period 1	Period 2	Period 1	Period 2	Period 1	Period 2
A	5,7	<28.7%	>18.1%	>6.0%	>8.0%	>0.7%	<21.7%
B	5,7,11	<28.7%	>18.1%	>6.0%	>8.0%	>0.7%	<21.7%
C	5,7,11	<28.7%	<18.1%	>6.0%	>8.0%	>0.7%	>21.7%
D*	5,7,11	>28.7%	>18.1%	<6.0%	>8.0%	<0.7%	<21.7%
E*	5,7,11	>28.7%	<18.1%	<6.0%	<8.0%	<0.7%	>21.7%
F*	5,7,11	<28.7%	<18.1%	>6.0%	<8.0%	>0.7%	>21.7%
BC	5,7,11	17.7%	11.0%	17.6%	37.2%	0%	0%

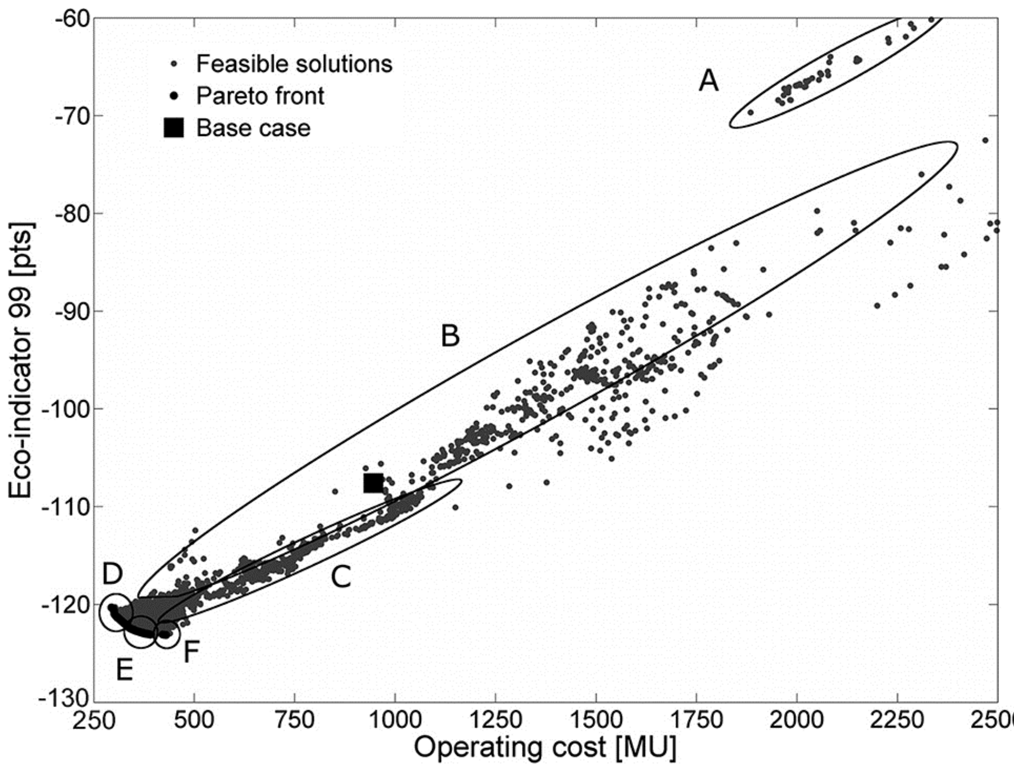

Figure 4-8 : Optimization results for scenario 1 of CS2 (five products P1–P5 in two production periods P1P2-P3P4P5, 12 waste streams [Table 4-II], two batch distillation columns, no azeotropes). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points and the base case solution are highlighted. Groups of similar mixing solutions (A to F) are identified and their description is provided in Table 4-IV.

The optimization results for the three different multiperiod configurations are summarized in Figure 9 (more details are also provided as Appendix J in Figure 8-13 and Figure 8-14, Table 8-XI and Table 8-XII). From Figure 4-9, it is evident that the impact of the production planning can be significant, especially when it is combined with a flexible waste mixing policy. More specifically, when the production planning changes and the waste mixing policy is not adjusted accordingly, the operating costs are reduced by only 20% at maximum (i.e., going from base case 1 to base 3 in Figure 4-9), while a total reduction of 100% would be possible, leading also to a source of profit in some extreme cases (i.e., Pareto front of the third multiperiod configuration). Similarly, the combination of a flexible waste mixing policy with an appropriate production planning can lead to an improvement of approximately 40% in the environmental performance of the system, compared to a respective reduction of only 8% at maximum, when the change in the production planning is not followed by a respective change in the waste mixing policy.

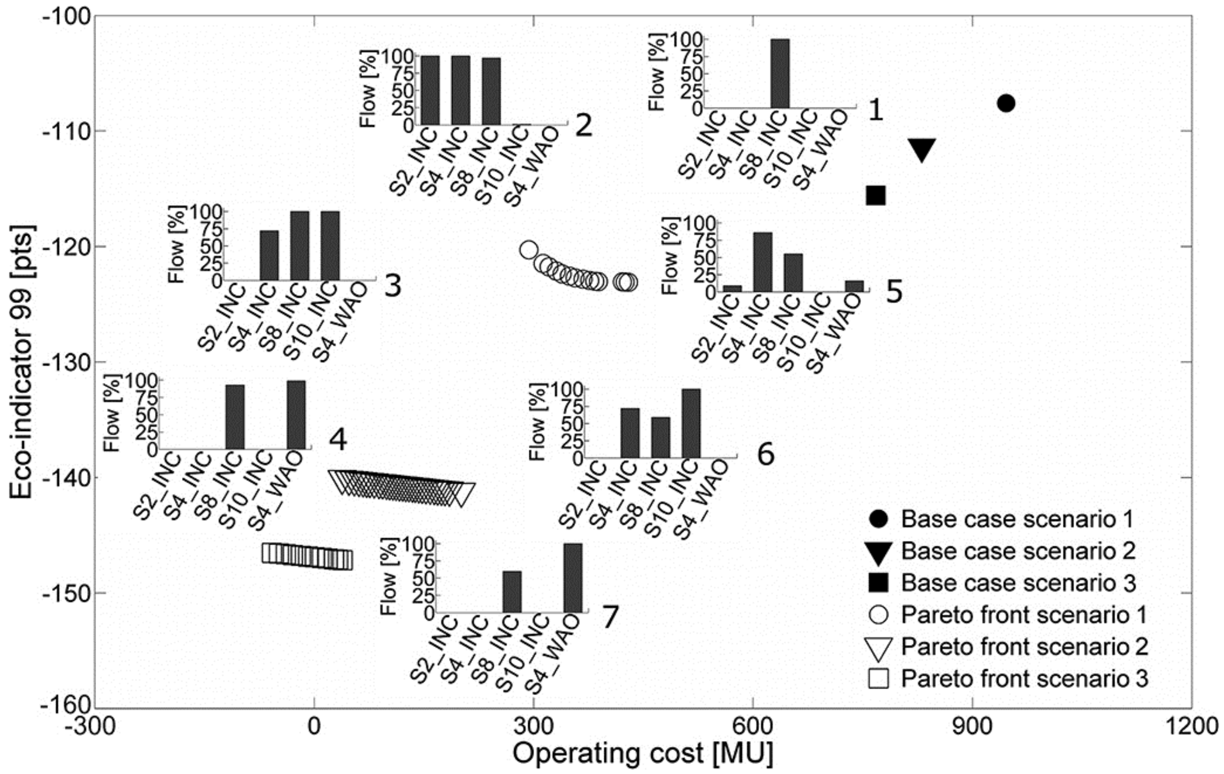

Figure 4-9 : Pareto fronts for scenarios 1 to 3 of CS2. For each scenario the anchor points of the Pareto fronts (i.e., optimal operating cost or Eco-indicator values) are described in detail with the help of bar charts (1: base case, 2: best operating cost for scenario 1, 3: best operating cost for scenario 2, 4: best operating cost for scenario 3, 5: best Eco-indicator99 for scenario 1, 6: best Eco-indicator99 for scenario 2, 7: best Eco-indicator99 for scenario 3). The operating cost is given in arbitrary monetary units (MU).

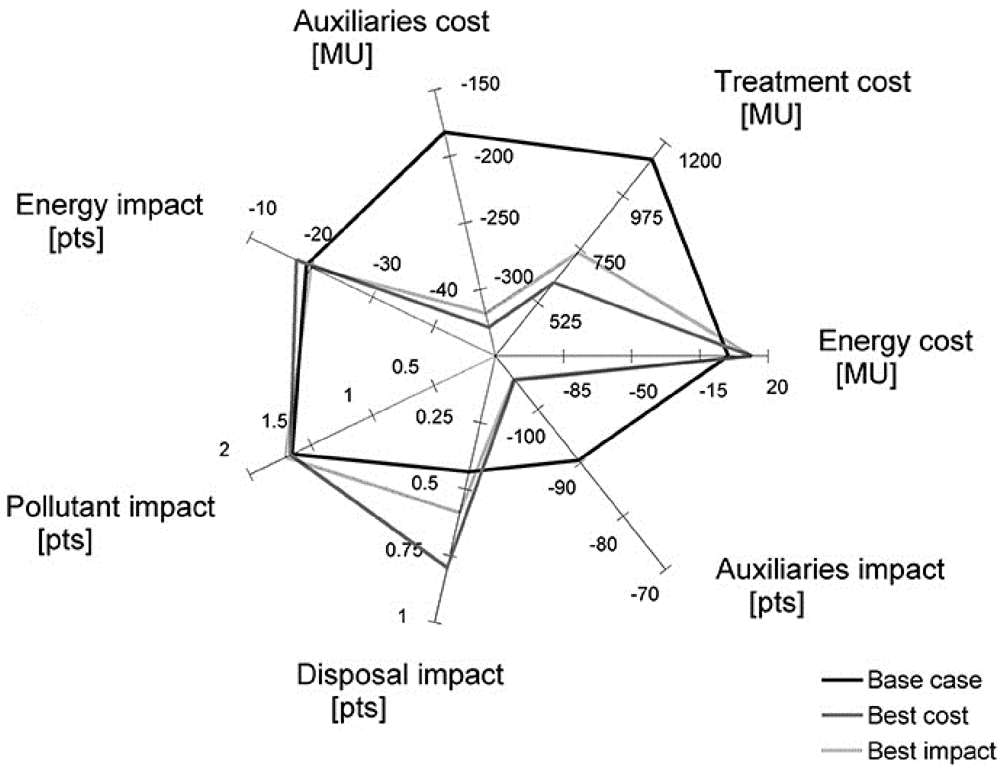

Figure 4-10 : Decomposition of operating cost and Eco-indicator values for scenario 1 of CS2. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas, steam). Pollutant impact: emissions to air, water and soil from the primary waste treatment units (DIST, INC, WAO, WWTP). Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 4-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units.

Analyzing the results of Figure 4-9 in more detail, it is interesting to note the distribution of streams 2, 4 and 10, which were originally treated in the WWTP according to the base case scenario (Table 4-II). Depending on the multiperiod configuration, some of these streams are partially used in the INC to replace fresh water for regulating the flue gas temperature, together with stream 6 (not shown in Figure 4-9), whose bigger part is assigned to INC in all optimal solutions. Stream 6 can be advantageously treated in the INC compared to streams 2, 4, and 10 due to its higher organic content, while its salt content plays an important role for excluding it from WAO in most of the cases (e.g., when it is treated in the same period with stream 4 in the P2P3-P1P4P5 multiperiod configuration, stream 4 is advantageously sent to WAO due to its Na2SO4 content, which would cause higher environmental impact if emitted as SO2 in the INC). Moreover, comparing the best economic to the best environmental objective performance of the system, the partial treatment of stream 8 in

WAO is the main trade-off factor for reduced Eco-indicator 99 values. The necessary dilution of this stream due to its high salt content is effected by the streams with the lower salt content available in the same period.

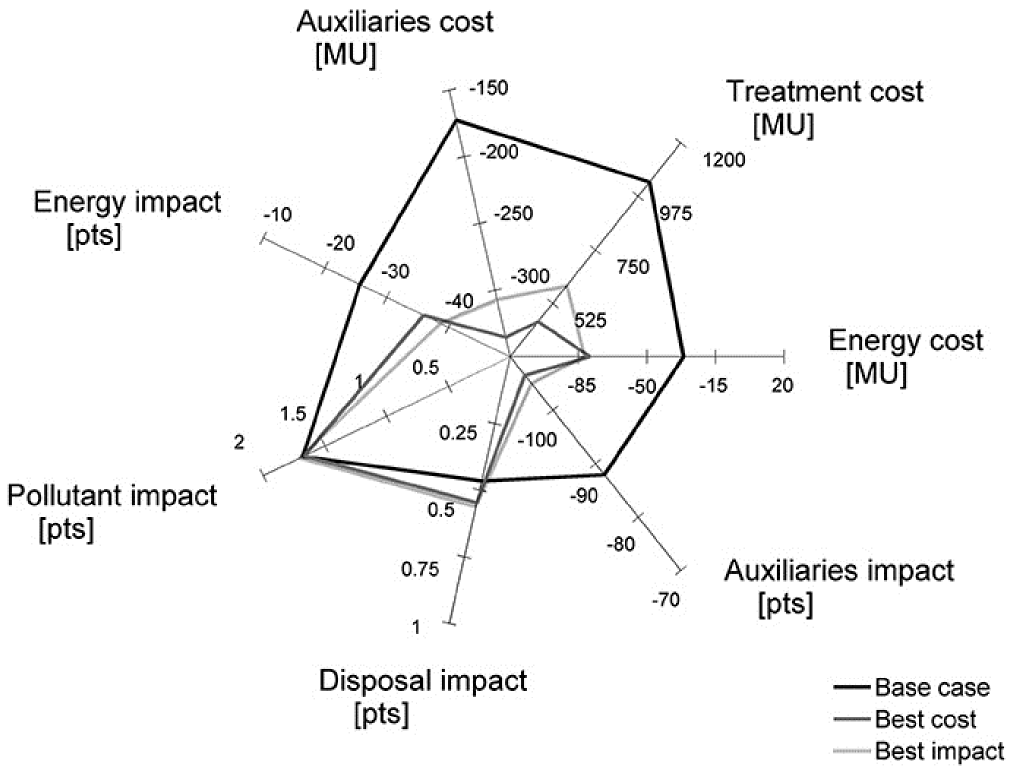

Figure 4-11 : Decomposition of operating cost and Eco-indicator values for scenario 2 of CS2. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas, steam). Pollutant impact: emissions to air, water and soil from the primary waste treatment units (DIST, INC, WAO, WWTP). Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 4-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units.

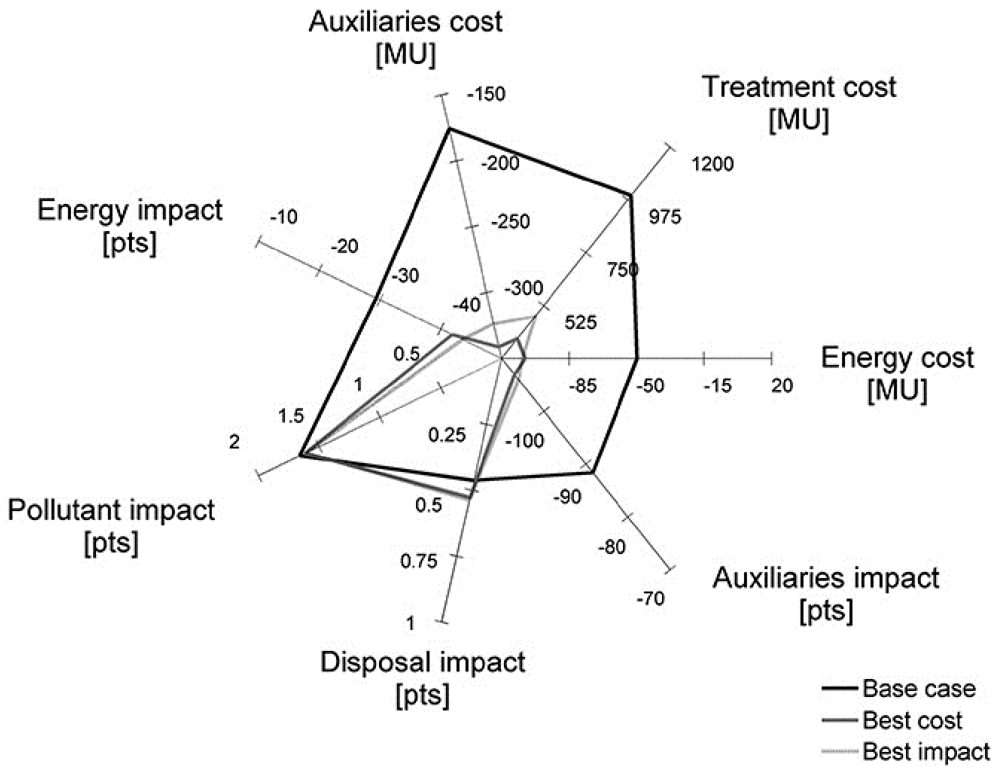

Figure 4-12 : Decomposition of operating cost and Eco-indicator values for scenario 3 of CS2. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas, steam). Pollutant impact: emissions to air, water and soil from the primary waste treatment units (DIST, INC, WAO, WWTP). Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 4-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units.

Figure 4-10, Figure 4-11 and Figure 4-12 present a decomposition of the operating cost and Eco-indicator 99 into subcategories for the three multiperiod configurations respectively. The categories of auxiliaries cost, treatment cost, auxiliaries impact are always improved compared to the base case. The pollution impact stays constant because any pollution reduction by transferring waste loads from WWTP to INC and WAO is compensated by the respective emissions of these units. On the other hand, in all configurations and Pareto optimal solutions the main trade-off to the base case appears for the disposal impact. This is due to the use of wastewater streams with high salt content in the INC, leading to a higher amount of solids to dispose (mainly in the form of Na_2O in the current study, see also Appendix L). Energy cost and energy impact are marginally increased in the first multiperiod configuration due to larger input flow rates to the INC from the transfer of waste loads originally assigned to the WWTP (i.e., mainly stream 6 in the second period), and therefore higher natural gas consumption. In the first period of the same multiperiod configuration, the additional waste loads of streams 2 and 4 in the INC only compensate the amount of fresh water needed for regulating the adiabatic temperature rise and therefore the overall input flow rate to the INC is similar to the base case. The respective values for the energy cost and energy impact in the other two multiperiod configurations are lower because of the assignment of P1 and P2 into two different periods, which results in reduced amounts of fresh water for regulating the adiabatic temperature rise (i.e., the adiabatic temperature rise is controlled by using mother liquor from the plant), and therefore in higher steam production due to less energy losses for fresh water evaporation. Here, it should be noted that a constraint in all scenarios and the base case is that mother liquor from the plant is not allowed to be used in combination with fresh water; that is, only one of them can be used for regulating the adiabatic temperature rise. As already mentioned, neither the economic and environmental impact nor the energy generation benefit from the mother liquor is allocated in the performance of the system.

The results of CS2 indicate the potential of considering an integrated design of production planning and waste management, especially when an intermediate waste storage policy is to be avoided. Of course, the practical realization of this potential should consider limitations in transportation pipes for distributing the waste flows to each treatment unit. Extreme piping can be reduced by buffer tanks for mixing and storing waste loads before the treatment in the respective unit, which however implies chemical compatibility.

4.5 Conclusions

This study analyzed the potential of integrated liquid waste management in chemical batch plants by examining flexible mixing policies and the impact of multiperiod production planning. In this context, multi-objective optimal solutions from cost and environmental perspective according to Pareto fronts were identified and compared to the respective base cases of limited mixing policies, which is a common practice in industrial systems. The multi-objective optimization of this study was facilitated by the use of previously developed LCIA models based on industrial data to describe emissions and utility consumption of the incineration, wet air oxidation, wastewater treatment plant, and distillation units of the waste management system. The complexity of real operations was considered through addition of industrial operating constraints for every treatment process, while emission limits according to environmental legislation were also used as overall terminal constraints.

This optimization framework was applied to two case studies, representing a full-scale scenario with general waste streams from the industrial system and a small-scale scenario with waste streams from specific batch processes and two-period planning scenarios. In the first case study, the results indicated a potential for operating cost reduction of 20% and environmental impact reduction of 10% compared to the industrial base case. It was also shown that continuous instead of batch distillation for solvent recovery can further increase these savings and that identification of azeotropic mixtures can be crucial for robust decision making. A general trend is that redistribution of the waste loads through more flexible mixing policies can be advantageous, especially in the direction of decreasing the use of fresh water and auxiliaries, for example, by shifting aqueous wastes from the wastewater treatment plant to the incineration units, where they can be used to regulate the temperature of the flue gas. The quantitative realization of such general heuristics, however, is governed by complicated interactions between parameters like basic treatment unit costs, auxiliary costs, disposal and emission impact, and even discrepancies between solvent prices and environmental benefit from their recovery. Therefore, the extent of waste redistribution is not necessarily leading to "win–win" optimal solutions but to economic–environmental trade-offs.

The problem becomes ever more challenging when it is integrated with the problem of multiperiod planning. Although in this study a framework for simultaneous optimization of multiperiod production planning and waste management has not been proposed, the effect of production planning on waste management was investigated in the second case study. There, it was demonstrated that even simple decisions about two-period planning of five batch processes can have a significant effect on waste availability, which can be treated with flexible mixing policies to increase operating cost savings and decrease environmental impact up to five times. Besides the trade-offs in waste management decisions identified in the first case study, additional critical factors of the production planning include the number of waste streams, which increases the mixing scenarios and therefore the optimization potential, the extent of generation of similar types of waste in the same production period, and the availability of waste storage, which, however, has not been addressed in this case study.

The results of this study show that the operating cost and environmental impact savings potential of flexible waste management systems is worth being further analyzed in various directions. First, the optimization of an integrated framework consisting of waste management, production planning, and possibly heat integration can increase even further the savings potential. Naturally, this integrated framework, apart from the individual constraints of its components, will have to comprise additional constraints or penalties for complex and impractical structures, in order for the solutions to meet industrial applicability standards. To this end, it is important to differentiate between grass-roots and retrofit design. Clearly, grass-roots design offers more degrees of freedom both to chemical production and service companies, in this case waste management and power plants, to exploit the potential of such an industrial symbiosis framework. From the service companies' point of view, this is because of the infrastructure that can be designed to avoid overcapacities and allow flexible piping installation that is necessary for dynamic decision making, considering diverse waste mixing policies. From the chemical production point of view, flexible multipurpose equipment and storage policies are required to fully exploit the benefit of a dynamic operation mode that will enhance an optimized matching between chemical waste production, energy recovered from waste management, and heat integration with the power plant. It is well accepted that considering these issues in early design phases significantly enhances the degree that such integrated frameworks can be implemented. This becomes even more evident when not only cost but also life-cycle environmental impacts are considered. This is not only because important degrees of freedom may be fixed in cost oriented optimal designs that are difficult to be reset in later retrofit designs considering also life-cycle impacts, but mainly because of the collaboration environment that has to be built between the partners of this industrial symbiosis network and that is crucial to maintain an optimal operation according to commonly decided and accepted goals in a multicriteria analysis. Of course, it should be clear that the presented integrated framework is also applicable in retrofit design of existing networks of chemical production plants and service companies. The aforementioned advantages of the grass-roots design may not be achieved to the same extent, but modifications in operation and design can be systematically investigated looking for “win–win” solutions for all the partners of the industrial network based on a higher degree of integration and an agreed multicriteria scope.

This work can be further extended by incorporating more detailed models for life-cycle inventories of the waste management and the chemical production processes (e.g., for energy consumption and solvent recovery in distillation as function of the composition of waste streams and not only of waste loads). Another direction could be to introduce stochastic waste loads and consider in the multi-objective optimization framework indices for operational flexibility in process design (Swaney and Grossmann, 1985). This would allow a shift from a hierarchical to an integrated approach for design and planning in waste management systems. Based on the results of the second case study, it is expected that increasing the degrees of freedom in the mixing policy along with an integrated framework for design and planning can significantly improve the obtained solutions. Furthermore, in our current work, the presented framework is modified to allow real-time optimization for scheduling of the waste management system on the basis of monitored process variables and forecasted waste streams in moving time windows.

To meet all these methodological challenges, the design and application of efficient mixed-integer-nonlinear programming algorithms ensuring sufficiently good approximations of the multi-objective Pareto fronts is indispensable. To this end, the multi-objective nature of the optimization problem can be enhanced by eliminating aggregated indicators (e.g., by decomposing the Eco-indicator into its elementary categories), in order to identify the dominating environmental impacts for the definition of the Pareto fronts. This will remove from the analysis the sometimes subjective nature of the aggregated environmental indicators and will also reduce the data requirements, since no data will have to be collected for those environmental categories that do not significantly contribute to the search for optimal solutions.

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Chapter 5

5 Global evaluation of energy consumption in a batch chemical plant

5.1 Introduction

Over the last decades increase of the energy cost and a better awareness of environmental impact of chemical industry modified the way chemical manufacturers managed the development and the production of their products. This evolution extended the framework of chemical activities to take these new problems into account and not only to focus on reactions and separation processes. Changes took place gradually and different methods were developed to integrate these new challenges.

In particular for the batch chemical plants, the application of heat integration is analyzed by several authors who applied an optimization process for heat recovery on a set of given production schedules: Corominas et al. (1994) defined a mathematical formulation for reducing the total energy requirements of a production schedule by matching streams through an exhaustive comparison of all combinations of hot and cold streams. Feasible matches are selected and an optimization of the exchange time is performed for each pair of streams by the introduction of delay time to increase the heat recovery under the constraints of the production schedule. Grau et al. (1996) enriches this optimization procedure by adding in the generation of production scheduling some penalties for changeover in the production lines by calculating a pollution burden due to the treatment of waste generated in set-up and cleanup tasks between campaigns of different products. Once a set of optimized schedules is generated the heat integration optimization starts to reduce the utility consumption following the procedure of (Corominas et al., 1994).

Adonyi et al. (2003) modifies the scheduling problem by integrating the heat integration as slave problem avoiding the two optimizations procedures of the previous authors. An S-graph method is developed to define for each solution of the production schedule a heat integration solution. The makespan of the schedule is then not more optimized but is considered as an upper constraint while the utility consumption is used as objective function. However, this approach focuses only on the production and neglects others energy consumers associated with the production of chemicals, i.e. the treatment of wastes generated by the production itself and the generation of the utilities.

This extension of the energy optimization is defined under the concept of Total Site Analysis (Dhole and Linnhoff, 1993) where heat sources and heat sinks of a plant are identified and the recovery is optimized with the help of the pinch analysis. The steam network is used as mean to transfer the energy from the heat sources to the sinks. Introduction of environmental impacts, such as CO_2 emissions in multi-objective optimization ensures the development of solutions compatible with environmental regulation (Klemeš et al., 1997). These studies only consider the utility network as source of savings and do not integrate some factors influencing the energy requirements of the different plant units.

The influence of the change in the energy demand over the time can be solved by using a multi-period approach. Marechal and Kalitventzeff (2003) study the utility network of a chemical plant with discontinuous processes. The processes are decomposed into several intervals where the energy loads can be considered as constant. Then by superposing, the intervals periods with constant loads can be created. For each period heat integration by pinch analysis is performed and different kinds of technology are selected to fulfil the requirements. The size of the different types of technology is fixed for all the periods of one solution and only an on/off mode is available to modify the use of one technology during the different periods. Summation of the operational cost of the different periods is used to evaluate each solution.

Wassick (2009) presents an example of enterprise-wide optimization including mid-term scheduling for the production and the waste treatments for an existing plant with defined waste treatment facilities and utility generation systems. A resource-task-network model is used to find optimal solutions according to an economical objective function. The horizon is divided in discrete time intervals with duration of one day. Different storage possibilities (tank, tank truck, etc.) are considered for waste management and raw materials but as resources and not as physical entities.

Halim and Srinivasan (2011) integrate heat integration and wastewater reduction in a scheduling problem. A State-task network is used to solve the problem based on a sequential methodology. To generate different optimal solutions an integer cut method is used which adds different constraints to the scheduling formulation to minimize the makespan. Once the solution is defined the process is split into two parallel runs: the first performs a heat integration analysis optimizing the heat recovery between processing tasks in the same time slot and the second analyzes the possibilities of reusing wastewater between cleaning tasks of the same time slots using the necessary fresh water to dilute the wastewater streams in order to keep contaminants concentrations below a certain value.

The present study enriches the system boundaries and focuses on the optimization of the energy consumption for a modeled chemical batch plant including production processes (see Chapter 3), waste treatments (see Chapter 4) and the utility generation system. These subsystems are integrated into a mathematical framework for operating cost calculation and environmental impact assessment. Multi-objective optimization is performed to investigate the more cost effective and environmentally benign ways to plan the production campaigns by considering simultaneously waste management and utility generation in a multi-periods analysis.

The rest of the chapter is structured in the following way. In section 5.2, the model of the synthetic plant is described, the optimization framework including the mathematical formulation of the problem as well as the different scenarios are presented. In section 5.3, the optimization results are presented and the influence of multi-periods, the environmental impact and the difference of the process energy requirements is thoroughly discussed. Finally, section 5.4 summarizes the main conclusions and identifies interesting research directions for future studies.

5.2 Method

5.2.1 Structure of the synthetic plant

The aim of the method presented here is to optimize the utility use at plant level by including all the main elements involved in the production of chemical products (production processes, waste treatments and utility generation system connected by their respective mass and utility flows) in a global multi-objectives and multi-periods evaluation. Several optimizations are performed by changing some evaluation parameters on the same system.

The production processes are considered as already optimized and the different steps of the recipes are not modeled. The batch processes are characterized by continuous mass and utility flows calculated by summing all specific flows of one batch divided by the cycle time. This allows for constant utility requirements and waste generation per unit of time for the next steps of the analysis where continuous operations are considered. The utility requirements include steam, cooling water, water, deionized water and electricity. Brine consumption was modeled as water and electricity consumption. Data are obtained from the energy analysis of five chemical processes representing two production buildings (see Chapter 3). Raw materials, final products and labor cost are not integrated in the analysis as the production processes are considered as fixed. No emissions to the environment are considered for that part of the plant.

The waste management system used in this analysis is described in Chapter 4 and is composed of one incineration unit (INC), a wet air oxidation reactor (WAO), a wastewater treatment plant (WWTP) and two batch distillation columns (DIST). The unique difference compared to the system defined in the previous chapter is the addition of a methanol flow in the WWTP unit to have more flexibility in the treatment of waste streams with a low biological oxygen demand and a high organic carbon contain. No waste storage is considered and waste streams have to be treated in the same period in which they were generated.

The utility generation system is defined according to the work of Bolliger (2010) based on a real utility network and integrating a steam boiler, a fuel source (natural gas), a compressed air network, a deionized water network, an industrial water source which is used as cooling source too, an electricity grid and a steam network. The connections between the different units of the global system are given in Figure 5-1. For each utility unit emissions, auxiliary and utility consumptions/productions are defined according to data from ecoinvent database or from industrial sources (see Appendix M, Table 8-XIII) in order to add the contributions of the utility system in the calculation of both economic and environmental indicators.

The steam cycle presented in the work of (Bolliger, 2010) is replaced by a unique steam turbine because only 6 bar steam is used in the synthetic plant and one turbine is enough to reduce the pressure form 62 to 6 bars and to produce electricity. The 62 bar steam is produced by the incineration unit and the steam boiler.

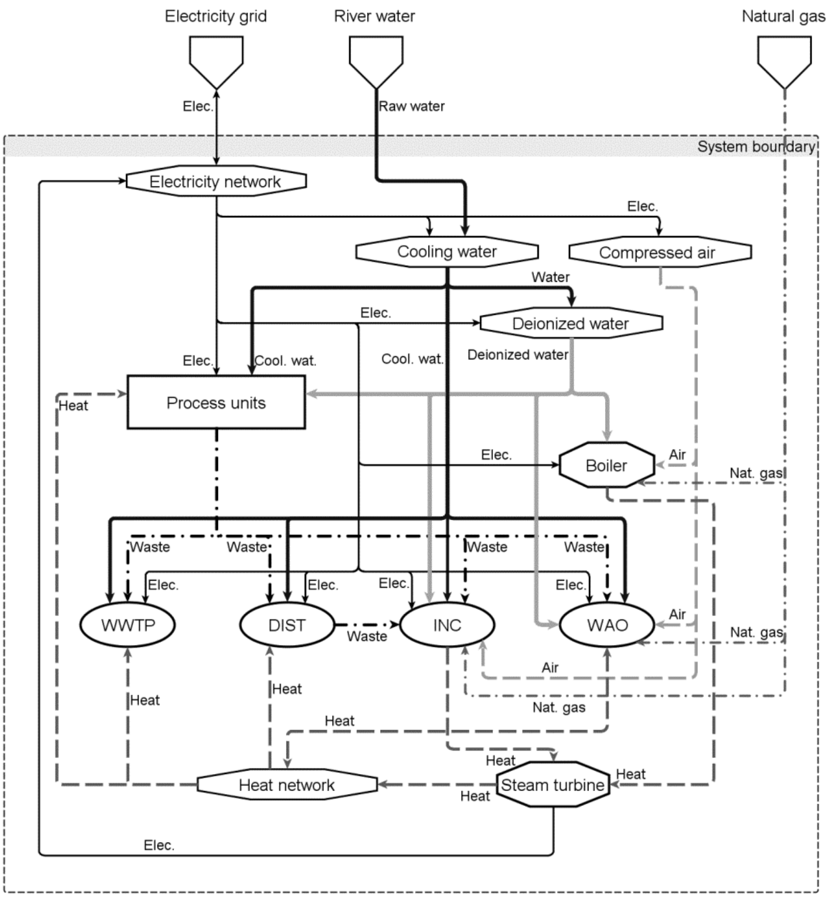

Figure 5-1 : Superstructure of the global system including the waste treatments units, the production buildings and the utility generation units. The different types of lines indicate the different types of utilities used in this system.

5.2.2 Heat integration

The models are integrated into the computation system Osmose developed at the Industrial Energy Systems Laboratory (LENI) at EPFL. This tool is designed to perform energy analysis for industrial cases studies using different softwares and models in a unique framework. One of the most interesting capabilities of Osmose is the possibility to perform heat integration based on the results of the models involved in the analysis. The heat integration uses the pinch technology to determine the maximal heat recovery between the existing energy streams and finally the minimal utility consumption. The respective capital costs are calculated only for this optimal heat recovery solution. To perform the pinch analysis an inventory of energy requirements is necessary with the following information: inlet and outlet temperature of the stream and amount of energy exchanged. Table 5-I presents the different energy flows identified in the system.

As already mentioned batch processes are considered as continuous with constant energy requirements per unit of time. This simplifies the heat integration since, otherwise, batch operations would have to be divided into a large number of periods with small duration and the heat integration would have to be performed through pinch analysis for each period leading to a large number of solutions with a high diversity in the matching of streams. On the other hand the production buildings of this study are multiproduct plants (or flowshop). Each product has its own production line and each operation is performed in a unique equipment. This leads to a constant operation planning which is independent of the number of processes running at the same time in the building. Furthermore as all processes are running at the same time the overall energy requirement is smoothed over the time reducing the influence of peaks.

The thermal data of the system are given in Table 5-I. Streams undergoing several types of heat transfer (like radiation-convection, latent-sensible heat exchange) are decomposed into several streams according to the specific type of heat exchange. For example, steam heating is decomposed into two hot streams, one for the steam condensation at constant temperature and a second one for the subcooling from the condensation temperature to the normal boiling point.

A further simplification of the energy integration problem refers to the thermal characteristics of the energy streams from the production processes. These are defined in terms of utility characteristics (see last line of Table 5-I), namely hot requirements are considered as 6 bar steam consumption and cold as cooling water use. For example, the heating requirement is defined not as the temperature increases in the process side but as the steam condensation on the utility side allowing the addition of different heat demands of one process into a unique one. Therefore, heat integration is not performed between production process streams.

Table 5-I : List of energy streams involved in the waste management system and in the utility generation units (rad. = radiation, conv. = convection, T_{evap} = vaporization temperature of organic solvent, T_{adia} = adiabatic temperature, $T_{preheat}$ = preheating temperature, T_{in} = input temperature of the stream, T_{out} = output temperature of the stream). The streams defined as utility consumptions consumption are highlighted in bold and their characteristics are temperature of saturated steam as T_{out} and temperature of normal boiling point of water for T_{in}.

Unit	Subunit	Stream description	Type	T_{in} [°C]	T_{out} [°C]	$\Delta T_{min/2}$ [°C]
DIST	**condenser**	**vapor condensation**	**hot**	$\mathbf{T_{evap}}$	$\mathbf{T_{evap}}$	**2**
DIST	**boiler**	**solvent evaporation**	**cold**	**159**	**159**	**3**
			cold	**100**	**159**	**3**
INC	combustion chamber	flue gas cooling (rad.)	hot	T_{adia}	T_{adia}	10
		flue gas cooling (conv.)	hot	T_{adia}	370	10
INC	quench	flue gas cooling	hot	370	80	2
INC	scrubber	flue gas cooling	hot	80	65	2
INC	denox	flue gas preheating	cold	65	310	5
INC	denox	flue gas cooling	hot	310	95	5
INC	denox	nat. gas combustion (rad.)	hot	880	880	2
		nat. gas combustion (conv.)	hot	880	310	2
WAO	WAO reactor	inflow preheating	cold	25	$T_{preheat}$	3
		outflow cooling	hot	290	70	3
WAO	stripping column	ammonia stripping	cold	159	159	3
			cold	100	159	3
WWTP	-	heating purpose	cold	159	159	3
			cold	100	159	3
Boiler	combustion chamber	flue gas cooling (rad.)	hot	1000	1000	10
		flue gas cooling (conv.)	hot	1000	120	10
Cooling water	heat exchangers	cooling	cold	10	40	3
Process	**heat exchangers**	**heating**	**cold**	**159**	**159**	**3**
				100	**159**	**3**
		cooling	**hot**	**10**	**40**	**3**

The incineration unit offers the most possibilities of heat exchange comprising the gradual cooling of the flue gas (i.e., up to 65 ^{o}C) and the treatment of the nitrogen oxides in a specific unit (denox) that requires pre-heating of the flue gas (i.e., up to 310 ^{o}C) before a catalytic reaction with ammonia, followed by cooling and release to the environment. As the model of Seyler (2005) does not provide any detail about the degree of heat recovery, some thermal characteristics of the hot stream (T_{adia}) are defined from the flow rate of the flue gas, its composition and the temperature profile from the industrial partner.

The steam consumption in the distillation is given by the model of Capello (2005) and the thermal characteristics are described in Table 5-I following the same method as for the process requirement with 6 bar steam. As the model of Capello (2005) does not give any information about cooling conditions but only the final cooling water consumption, the cooling requirement is calculated here according to the maximal allowable temperature output for release of water in the river (i.e., 40°C), the input temperature of the water (i.e., 15°C) and a constant heat capacity of water (i.e., 4.18 kJ/kg K). These energy requirements are defined for each distillation unit separately.

The steam consumption for the wastewater treatment plant (WWTP) is defined by the model of Koehler (2006), following the same method as for the process requirement with 6 bar steam. The steam consumption is not detailed for the different processes in WWTP and the steam is assumed to be used in a total heat exchanger representing the WWTP overall steam requirements.

In the wet air oxidation unit (WAO) the output temperature of the reactant flow is 290°C in order to ensure a complete oxidation reaction. To reach that temperature the inflow has to be heated complementing the energy provided by the oxidation of the organic content in the reactor provides. Therefore, the preheating temperature of the inflow is calculated as the output temperature minus the adiabatic temperature rise of the oxidation reaction which is a function of the organic carbon concentration. Respecting the maximal organic carbon concentration allowed in the unit necessitates always a minimal heat requirement. The cooling requirements of the outflow (i.e., defined as an aqueous solution of sodium sulfate) are based on data of the industrial partner as the model of Koehler (2006) does not give any information about process conditions. The off-gas is normally treated by a catalytic reaction to eliminate volatile organic pollutants and carbon monoxide in a similar way to the denox subunit of the incineration process but due to the lack of information for the temperature profile these energy requirements are not included in the heat integration. The stripping column in the WAO unit corresponds to the ammonia stripping by steam after the oxidation treatment and the energy requirement of this subunit is a function of the nitrogen content of the waste stream. The stripping process is not detailed and the steam is assumed to be used in a jacketed vessel.

Cooling water and steam boiler are utility units used to fulfil the demand of the synthetic plant. Their contribution in the heat integration is defined after the maximal heat recovery is determined. A maximal capacity is defined for each utility generation unit (i.e., the maximal utility flow that the unit can provide) and this is based on data of the industrial partner (see Appendix M, Table 8-XIV).

Residual energy from heat integration cannot be sold outside of the system. This constraint is added to avoid the risk of designing utility units at their maximal capacity due to some potential benefit not linked with the system under study.

5.2.3 Mathematical formulation of the optimization system

For the synthetic plant described in the previous sections, a multi-objective optimization problem is solved in terms of economic and environmental objectives. The problem can be described as follows:

Given

1. A limited horizon for the production planning
2. An exact amount for each chemical to produce defined as a fixed number of production weeks
3. A list of waste streams associated to production processes with given composition/property characteristics

According to

4. A list of available technologies for utility generation with a variable size
5. A list of available technologies for waste treatments
6. Two objective functions (environmental and economic indicators)

Determine

The optimum production planning with respect to operating cost and environmental impact.

Due to interdependencies between the problem variables (e.g., the waste streams in one period are a function of the production processes running in that period, the energy requirements are a function of the process requirements and of the utility consumption/generation in the waste treatments units) the overall optimization problem is decomposed into two parts: one master problem representing the production planning (MINLP, solved with the help of a multi-objective evolutionary algorithm (Leyland, 2002, Molyneaux, 2002) and two slave problems for the waste mixing (MINLP, solved with the same evolutionary algorithm) and the heat integration ((LP, solved with simplex method), respectively.

The master problem is defined as a multi-objective optimization problem (eq 5.1). The horizon for the production planning is fixed at 6 months and the number of production periods varies from 4 to 6. The variables are the duration of each period (d_p, calculated as an integer number of weeks with a minimal value of 2 weeks per period (see eq 5.3)) which sum up to the duration of the planning horizon (eq 5.2). Moreover, if a production process is allocated to a certain period ($y_{p,h}$=1), it is produced throughout this period. Considering that every production process has to take place for a certain number of weeks within the horizon, the d_p variables of the production planning are further constrained (eq 5.4). The activity of each process (five processes in total, P1-P5, see also Chapter 4) in the different periods is determined by a binary variable (eq 5.10). The objective functions are the operational cost comprising the cost of the three parts of the system (i.e., production processes, utility generation and waste treatment, see eq 5.5) and the environmental indicator (eq 5.6), which can be one of the Eco-indicator 99 (Goedkoop and Spriensma, 2001), the Ecological Scarcity 97 (Ahbe et al., 1990) or the Cumulative Energy Demand (Jungbluth and Frischknecht, 2004).

The waste treatment processes of the waste mixing problem are listed in the section 5.2.1 and the operation constraints are presented in the section 4.3.2. The waste mixing problem variables are the flowrates of the waste streams to the different treatment units. Equations 5.12-5.15 have been already explained in section 4.2.1 (eq. 4.2-4.5). Here, the waste mixing is optimized only according to the operational cost of the waste treatment processes (eq 5.16). In the general procedure, the waste mixing was solved only once for each different waste mixing case: the number of possible waste mixing cases is given by the combinations of production processes and once an optimal solution is defined for each waste mixing case, the solution can be used in the global evaluation without the need of repeating optimizations of the waste mixing problem. This approach was possible because no variable of the waste mixing problem is also a variable of the planning problem and the number of combinations was relatively small.

The available energy utilities are defined in section 5.2.1. The heat integration problem is solved by minimizing the cost of the utility generation to fulfil the demand of the whole plant (eq 5.17) in each period, that is the composite curve is divided in a number of temperature intervals (n_q) which are used to compute heat balance between the hot and cold curves of the interval (eq 5.18). The objective function is described by eq 5.19 and eq 5.22.

The mathematical formulation of the global problem is given as follows:

Master problem (production planning)

$$\min_{d_p, y_{p,h}} OF_1, OF_2 \ s.t. \tag{5.1}$$

$$\sum_p d_p = H \tag{5.2}$$

$$2 \le d_p < H \tag{5.3}$$

$$\sum_p d_p \cdot y_{p,h} = PP_h \ , \forall\, h \tag{5.4}$$

$$\begin{aligned} OF_1 = \sum_p d_p \cdot \Bigg(\sum_k \Bigg(cf_k \cdot \sum_h y_{h,p} \cdot \sum_i q_{i,h,k,p} + \sum_m cf_m \cdot QU_{m,k,p}(q_{k,p}, c_{,k,p}) \Bigg) \\ + \sum_h \sum_m cf_m \cdot QU_{m,h,p} \cdot y_{h,p} + \sum_u \sum_m cf_m \cdot QU_{u,m,p}(R_p) \Bigg) \end{aligned} \tag{5.5}$$

$$\begin{aligned} OF_2 = \sum_p d_p \cdot \Bigg(\sum_k \Bigg(\sum_m ef_m \cdot QU_{m,k,p}(q_{k,p}, c_{k,p}) + \sum_n ef_n \cdot QE_{n,k,p}(q_{k,p}, c_{k,p}) \cdot \Bigg) \\ + \sum_h \sum_m ef_m \cdot QU_{m,h,p} \cdot y_{h,p} \\ + \sum_u \sum_n ef_n \cdot QU_{n,p,u}(R_p) + \sum_u \sum_n ef_n \cdot QE_{n,p,u}(R_p) \Bigg) \end{aligned} \tag{5.6}$$

$$q_p = \sum_k q_{k,p} \cdot \tag{5.7}$$

$$q_{k,p} = \sum_i \sum_h q_{i,h,p} \cdot y_{h,p} \tag{5.8}$$

$$c_{k,p} = \{c_{j,k,p}\} \tag{5.9}$$

$$d \in \aleph, b \in \{0,1\} \tag{5.10}$$

*Slave problem 1 (waste mixing) **

$$\min_{x_{i,k,p}} OF_p \quad s.t. \tag{5.11}$$

$$Q_{k,min} \leq \sum_i \sum_h q_{i,k,p} \cdot y_{p,h} \leq Q_{k,max} \tag{5.12}$$

$$\sum_k \sum_h q_{i,k,p} \cdot y_{p,h} = \bar{q}_i \tag{5.13}$$

$$\sum_i q_{i,k,p} \cdot c_{i,j,p} \leq \left(\sum_i q_{i,k,p} \right) \cdot \overline{c_{\iota,k}} \tag{5.14}$$

$$lb_{l,k} \leq g_l(q_{i,k,p}, c_{i,j,p}) \leq ub_{l,k} \tag{5.15}$$

with

$$OF_p = \sum_k \left(cf_k \cdot \sum_i \sum_h q_{i,h,k,p} \cdot y_{p,h} + \sum_m cf_m \cdot QU_{m,k,p}(q_{k,p}, c_{k,p}) \cdot \right) \tag{5.16}$$

*The integer variables are the decision parameters to send or not a waste stream to the distillation

*Slave problem 2 (heat integration) **

$$\min_{R_{1,p}} OF_p \quad s.t. \tag{5.17}$$

$$R_{q,p} = R_{q+1,p} + \sum_{r \in \alpha_q^{hot}} E_{r,p} - \sum_{s \in \alpha_q^{cold}} E_{s,p}\,, \forall q = 1, \dots, n_q \tag{5.18}$$

$$OF_p = cf_{hu} \cdot QU_{hu,p} + cf_{cu} \cdot QU_{cu,p} \tag{5.19}$$

$$R_{q,p} \geq 0, \forall q = 1, \dots, n_q \tag{5.20}$$

$$R_p = \left\{R_{1,p}, R_{n_q,p}\right\} \tag{5.21}$$

$$\begin{gathered} QU_{hu} = R_{n_{q,p}} / \Delta_{vap} H_{hu} \\ QU_{cu} = R_{1,p} / (Cp_{cu} \cdot \left(T_{cu}^{out} - T_{cu}^{in}\right)) \end{gathered} \tag{5.22}$$

*The input data for heat integration are defined in Table 5-I with the heat flows coming from the master problem and the slave problem 1

The optimization process is described in Figure 5-2 with the optimization levels and the decision nodes integrated in the global system.

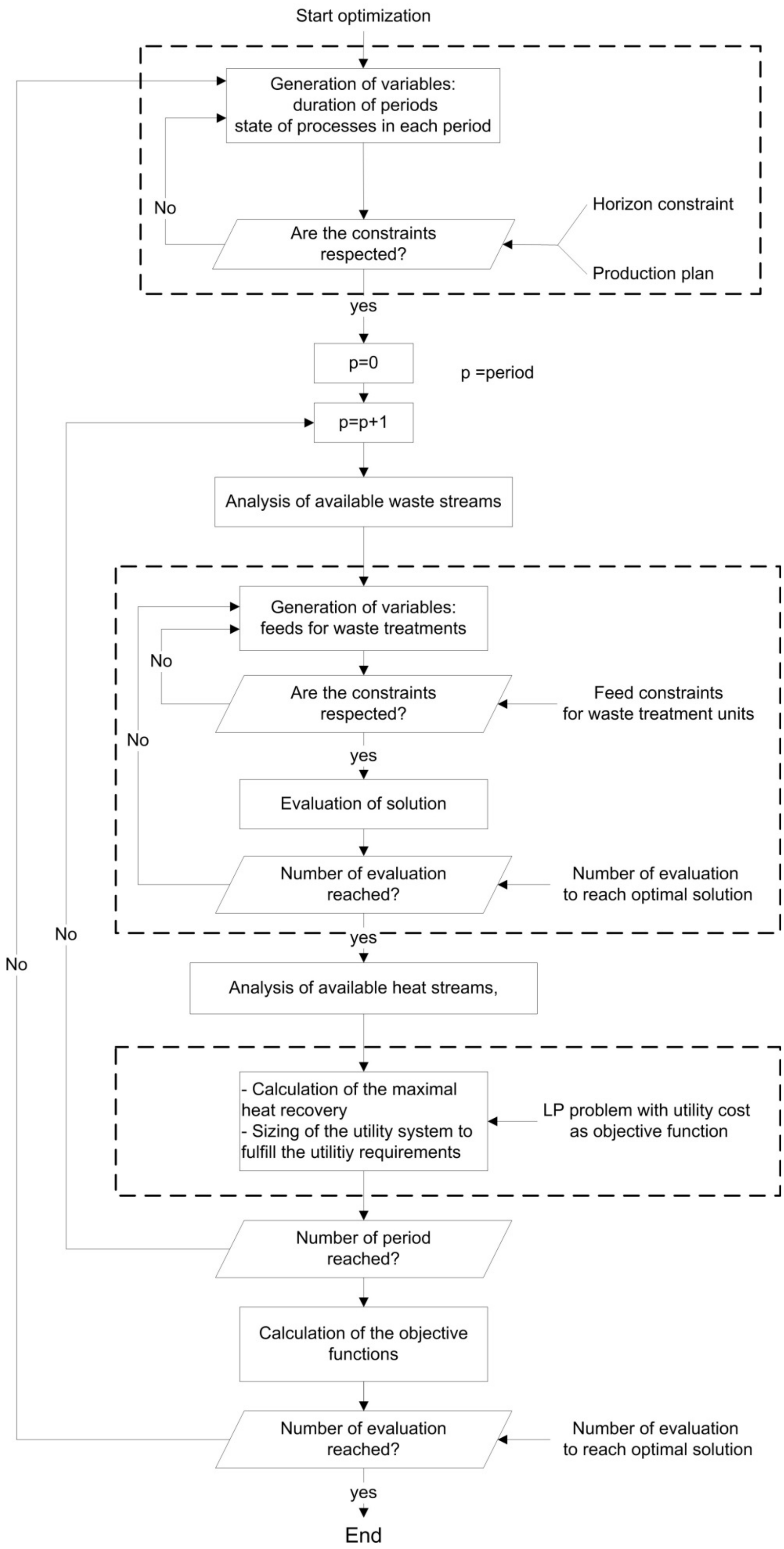

Figure 5-2 : Scheme describing the optimization process for the global system of production planning, waste mixing and generation of energy utilities considering heat integration. Dotted areas represent optimization parts.

5.2.4 Case Studies

Different optimizations scenarios are analyzed based on several parameters:

- Three different LCIA indicators (Eco-indicator 99 (ei99(H,A)), Ecological Scarcity (UBP) and Cumulative Energy Demand (CED)) are tested to represent environmental impact in the multi-objective optimizations. The operating cost is always used for the economic indicator. This scenario will demonstrate the impact of the chosen environmental metric in the obtained optimal solutions.
- The horizon time is divided into 4, 5 or 6 periods. This scenario will demonstrate the impact of a more flexible planning, which is an intrinsic advantage of batch operations.
- The energy requirements for the production processes are defined according to the real measurements (including thermal losses) or to the results of a theoretical modeling based on recipe and process data. The difference concerns the steam and water consumption and is around 40% for steam and 50% for water. This scenario will demonstrate the importance of accurate energy modeling as proposed in Chapter 3.

Table 5-II : Description of the scenarios with their different characteristics

Scenario	LCIA indicator	# periods	Process requirements	Objective function in waste mixing
S1	ei99	4	real	cost
S2	ei99	5	real	cost
S3	ei99	6	real	cost
S4	UBP	4	real	cost
S5	CED	4	real	cost
S6	ei99	4	theoretical	cost

5.3 Results and discussion

5.3.1 Case 1: Comparison of scenarios (S1, S4, S5) with different environmental impact indicators

The influence of the environmental indicators on the optimization process was analyzed for the case of dividing the horizon in four periods (scenarios S1, S4, S5, see Table 5-II). This case has few feasible solutions (~1200) allowing the evaluation of all solutions and ensuring a representative comparison of data.

The optimization results for scenario S1 are given in Figure 5-3. Two Pareto optimal solutions are found and present a large improvement compared to the average values of all feasible solutions for both indicators (60% for environment impact and operational cost). Similar reduction for the other environmental indicators was observed (see Appendix N, Figure 8-18 and Figure 8-19) but in a smaller extent (10% for Ecological Scarcity, scenario S4, and 50% for Cumulative Energy Demand, scenario S5). The combination of processes in the different periods for the optimal solutions is given in Table 5-III. For all optimal solutions only three different combinations of processes have been determined if the diverse production planning scenarios are concatenated in three periods with the same duration of 8 weeks for each period (see also the explanatory example in Table 5-III).

The Pareto fronts of scenarios S1, S4 and S5 are presented in Figure 5-4. Normalization was applied for the environmental impact on the basis of the smallest value for each indicator.

Despite the differences in the methodologies the three environmental indicators are able to point to sets of common solutions. The common solution for all three scenarios corresponds to the optimal solution for operational cost. The second common solution is shared by the EI99 and the CED environmental indicator scenarios and the last two solutions are present only in one Pareto front, namely in the Pareto front of the CED indicator scenario and in the Pareto front of the UBP indicator scenario, respectively.

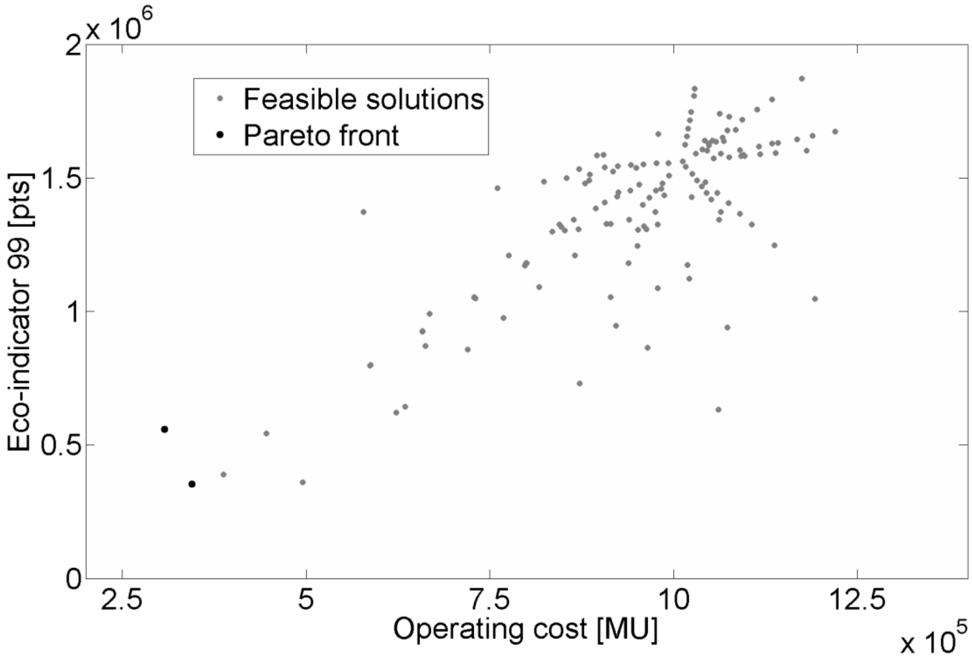

Figure 5-3 : Optimization results for S1 (4 periods with EI99 as environmental indicator and operating cost in arbitrary monetary units [MU]). Pareto optimal points are highlighted in bold.

Table 5-III : Pareto optimal solutions for scenarios S1, S4 and S5. The combination of processes in the different periods is given with the duration of each period (in brackets). Only unique combination of processes are shown with respect to the total number of weeks (see footnote[1]). EI = environmental indicator.

Scenario	Indicator	Period	Processes groups	Normalized value for EI
S1	EI99	4	P4 (8) ; P2P3P5 (8) ; P1P3P4 (8)	1.58
			P4 (8) ; P2P3 (8) ; P1P3P4P5 (8)	1.00
S4	UBP	4	P3 (8) ; P2P4P5 (8); P1P3P4 (8)	1.000
			P4 (8) ; P2P3P5 (8) ; P1P3P4 (8)	1.002
S5	CED	4	P4 (8) ; P2P3P5 (8) ; P1P3P4 (8)	1.35
			P4 (8) ; P2P3 (8) ; P1P3P4P5 (8)	1.02
			P3P4P5 (8) ; P2P3 (8) ; P1P4 (8)	1.00

[1] Each combination can produce several solutions which are given identical results. As example for the first solution of S1:
Solution 1: P4 (8) ; P2P3P5 (8) ; P1P3P4 (6); P1P3P4 (2)
Solution 2: P4 (8) ; P2P3P5 (8) ; P1P3P4 (4); P1P3P4 (4)

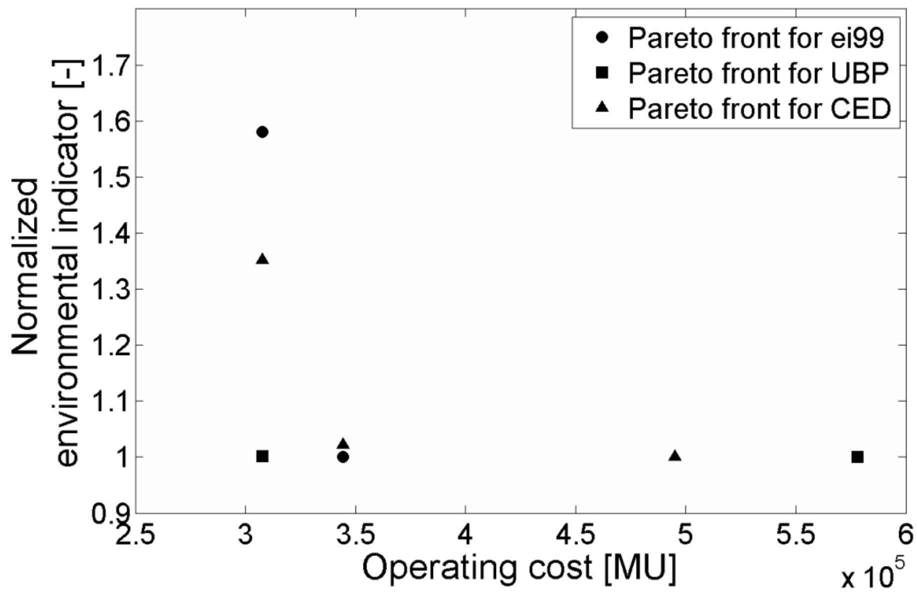

Figure 5-4 : Pareto fronts for the three scenarios (S1, S4, and S5) with different environmental indicators.

By looking at the different combination of processes the principal change between two optimal solutions is due to the displacement of one process from one period to another period. For the scenario S1, the process P5 of the period P2P3P5 was moved to the period P1P3P4. For scenario S4, the process P3 from period P2P3P5 was exchanged with the period comprising only P4. In the scenario S5, the same modification like in scenario S1 is done and for the third solution the process P1 of the period P1P3P4P5 was added to the period comprising only P4.

A general pattern for the optimal solutions in terms of operational cost comprises solutions with one period containing only one process, for example P4. This process is beneficial because it is composed of only two streams, a waste solvent for the distillation and a wastewater stream. As the wastewater treatment cost is relatively low and the regenerated solvent is important, the operating cost for this process is negative allowing a reduction of the overall cost of the processes combination. If P4 is combined with other processes comprising waste solvents also beneficial to be recycled (for example, P2 and P3), this benefit may not be realized due to limited distillation capacity.

For the scenario S1 as the process P5 is producing a mixture of organic solvents, the combination P1P3P4P5 generates too many streams for the capacity of the incineration compared to the P1P3P4 case, and now part of these streams have to be treated in the wet air oxidation unit. At the same time, since in this case more processes take place in the same period, the additional steam demand of period P1P3P4P5 is provided by an excess of natural gas in the steam boiler leading to a doubling of natural gas consumption and an increase of 40% of the energy cost (see Table 5-IV, Figure 5-5 and Figure 5-6). On the other hand, the important decrease of the environmental impact between these two cases is the reduction of electricity consumption due to the higher production of electricity from the steam boiler (i.e., using the excess of natural gas). This happens because of the relatively high cost of natural gas, the higher efficiency of the steam boiler compared to the incinerator for electricity production and the higher contribution of electricity in the environmental impact than the operation cost. Moreover, the steam production with the steam boiler implies more air compression and larger deionized water consumption resulting in an increase of 35% of the utility generation cost (see Figure 5-5 and Figure 5-6), while only a part of the electricity excess produced in the steam boiler is consumed by this additional air compression demand and pumping of water.

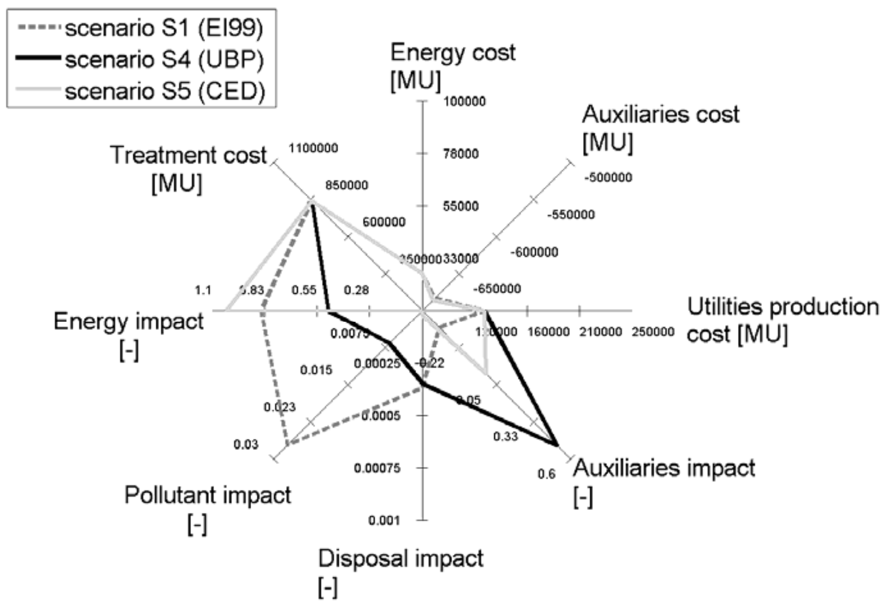

Figure 5-5 : Decomposition of operating cost and environmental impact for optimal cost solutions in scenarios S1, S4 and S5. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas). Pollutant impact: emissions to air, water and soil from the waste treatment units and utility generation units. Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 5-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units. Utility cost:

occupancy cost for utility production. For comparison purpose the environmental values are normalized according to the minimal value obtained in the optimizations.

A closer look at the scenario S5 leads to similar conclusions when CED is used as environmental impact indicator. Moreover, it reveals that a further improvement of the environmental impact along the Pareto front of S5 (i.e., having as a trade-off an increase of the operating cost) was achieved by merging P1 and P4 in the same period, reducing the number of processes in the period P1P3P4P5, which now becomes again P3P4P5. This shift of P1 to another period reduces significantly the organic waste amount available for the incineration unit but does not reduce in the same extent the energy requirements of the P3P4P5 block of processes. Therefore, the heat demand has to be covered again by the steam boiler increasing further the consumption of natural gas. Moreover, there is now no need for using the wet air oxidation to treat waste streams of P3P4P5 and the steam boiler has to compensate for this steam amount too. Additionally, the steam boiler in P1P4 is not any more necessary as process P1 provides sufficient amount of organic waste to cover the combined steam demand of P1P4 and partially the demand in electricity (i.e., this period becomes now an electricity consuming period, while P4 alone was an electricity producing period) but the effect of this additional electricity consumption is significantly lower than the effect of electricity production in the period P3P4P5.

In scenario S4, a significant improvement is observed in the operation cost with almost negligible deterioration of the environmental impact. In this scenario, the combination P2P3P5 generates too many organic waste streams in the same period and a stream of process P2 which is normally incinerated in the period P2P4P5 has to be sent to the wet air oxidation in the period P2P3P5. Moreover, when P4 is produced alone in one period, steam production is required by the steam boiler because the only organic waste stream available in the period P4 is regenerated instead of being burnt. On the contrary, when P3 is produced alone in one period, it generates enough steam through waste incineration. This change of heat source reduces the natural gas consumption in the optimal environmental solution by 88% (see Table 5-IV). On the other hand, the electricity produced by the steam boiler during period P4 is higher than the demand and no external power is needed. As the waste incineration unit is less efficient in the energy recovery, the electricity production in period P3 must be compensated with power from the external network. Moreover, the reduced organic waste in period P2P4P5 decreases the fuel availability for incineration and the production of electricity which is also compensated by external power. These two effects lead to an increase of electricity consumption in the optimal environmental solution by 80% (see Table 5-IV). These two effects almost cancel out each other in terms of environmental impact, which can be also observed by comparison of the energy impact in Figure 5-5 and Figure 5-6, but demonstrate a small benefit in the energy cost for the best environmental impact solution. But in the same figures it can be observed that overall the operation cost is significantly higher in the best environmental solution due to the auxiliaries and treatment cost. The auxiliaries cost increases mainly because of not sending P2 to wet air oxidation and losing the benefit of the respective by-products. The treatment cost increases due to the same reason: the stream of process P2 treated in the incineration generates more solid wastes which have to be disposed.

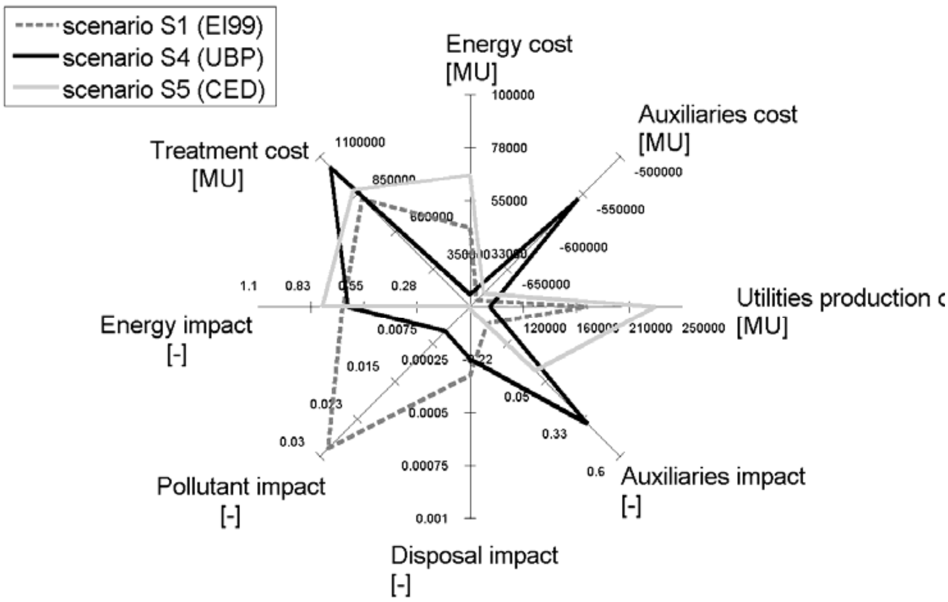

Figure 5-6 : Decomposition of operating cost and environmental impact for optimal environmental solutions in scenarios S1, S4 and S5. Negative values indicate monetary gain or environmental benefit. The operating cost is given in arbitrary monetary units (MU). Energy cost or impact: energy utilities (electricity, natural gas). Pollutant impact: emissions to air, water and soil from the waste treatment units and utility generation units. Disposal impact: emissions and utilities/auxiliaries used in the final disposal units (see Figure 5-1). Auxiliaries impact or cost: chemical auxiliaries used in the primary waste treatment units. Treatment cost: occupancy cost for both primary treatment and final disposal units. Utility cost: occupancy cost for utility production. For comparison purpose the environmental values are normalized according to the minimal value obtained in the optimizations.

Table 5-IV : Consumption of electricity, cooling water and natural gas as external supply for optimal solutions (operating cost and environmental impact) for scenarios S1, S4 and S5.

		Natural gas [kg]	Electricity [kWh]	Cooling water [m^3]
Optimal cost solution	EI99 UBP CED	52497	80152	284959
Optimal environmental solutions	EI99	108670	61023	299844
	UBP	6483	145294	277147
	CED	176844	59611	314879

5.3.2 Case 2: Comparison of scenarios (S1, S2, S3) with different number of periods

The results of the optimization scenarios with different number of periods are given in Figure 5-3, Figure 8-20 and Figure 8-21 in the Appendix O. The performance domain of feasible solutions in Figure 8-20 and Figure 8-21 stays the same but the number of possible solutions increased with the number of periods. Their Pareto fronts are presented in Figure 5-7 for comparison purposes. The Pareto fronts of the scenarios S2 and S3 are composed of the same solutions as described in Table 5-V. S2 and S3 have both the two optimal solutions of S1 in addition to other solutions. These other solutions are defined by the same combination of periods with variable durations creating a straight line as Pareto front.

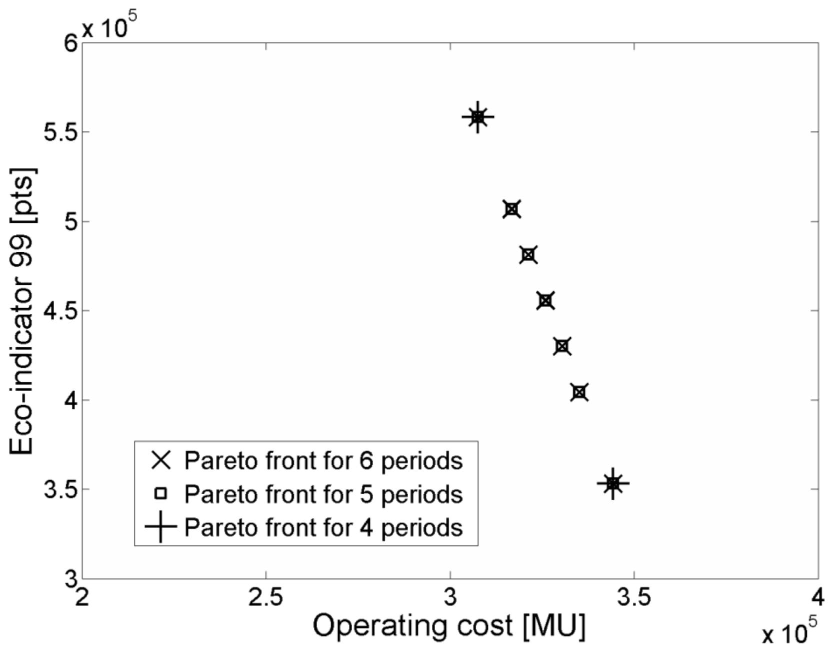

Figure 5-7 : Comparison of Pareto fronts for the scenarios S1, S2 and S3 with different number of periods.

Table 5-V : Pareto optimal solutions for the scenarios S1, S2 and S3. The combination of processes in the different periods is presented along with the duration of each period (in brackets). Only unique combinations of processes are shown with respect to the total number of weeks.

Scenario	Period	Processes groups	Normalized value for EI99
S1	4	P4 (8) ; P2P3P5 (8) ; P1P3P4 (8)	1.58
		P4 (8) ; P2P3 (8) ; P1P3P4P5 (8)	1.44
S2/S3	5/6	P1P3P4P5 (2); P2P3 (2); P1P3P4 (6); P2P3P5 (2); P4 (8)	1.36
		P1P3P4P5 (3); P2P3 (3); P1P3P4 (5); P2P3P5 (5); P4 (8)	1.29
		P1P3P4P5 (2); P2P3 (6); P1P3P4 (2); P2P3P5 (6); P4 (8)	1.22
		P1P3P4P5 (2); P2P3 (6); P1P3P4 (2); P2P3P5 (6); P4 (8)	1.15
		P1P3P4P5 (4); P2P3 (4); P1P3P4 (4); P2P3P5 (4); P4 (8)	1.00

5.3.3 Case 3: Comparison of scenarios (S1, S6) with theoretical and real production process energy demand

The results of the optimization with the theoretical energy requirements for production processes are given in Figure 5-8. A comparison with Figure 5-3 shows a shift of the whole performance domain of solutions to smaller values for both operating cost and environmental impact, the latter having even negative values in the Pareto front. This shift was expected as reduced amount of energy requirements were considered in the optimization. However, with respect to the production planning profile of the solutions, the Pareto front is the same as for scenario S1, namely two optimal solutions with the same combination of processes (see Table 5-III). On the other hand, although the Pareto front is identical to S1, the domain of the feasible solutions demonstrates a different pattern. The solutions have an environmental impact in a narrower interval of values and some solutions have a relative position completely different from scenario S1.

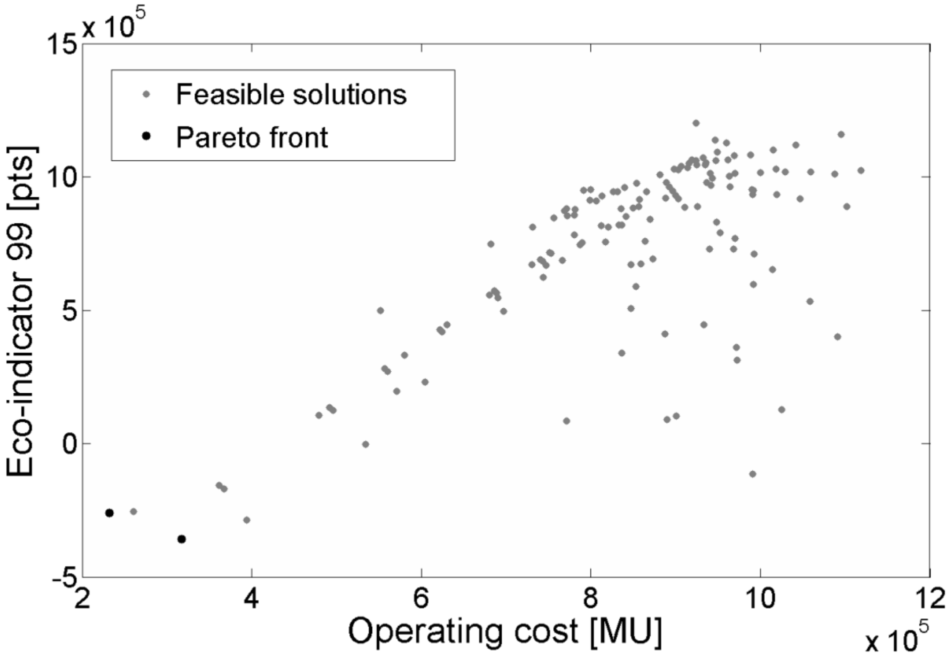

Figure 5-8 : Optimization results for S6 (4 periods with theoretical energy demand for the production processes, EI99 as environmental indicator and operating cost in arbitrary monetary units [MU]). Pareto optimal points are highlighted in bold.

The differences in raw energy consumption are provided in Table 5-VI. For the case of the optimal cost solution smaller energy requirements can be observed for all primary energy vectors. The smaller heat demand as a result of the smaller theoretical heat requirements reduces the use of the steam boiler and the respective electricity production. However, the reduction of the cooling duty implies less water pumping and less electricity required by the utility generation system. As the water pumping is one of the principal electricity consumers, the reduction in electricity demand is higher than the decrease of electricity production in the steam boiler.

The relative reduction of electricity is higher than natural gas due to the fact that the electricity required for the overall system depends in a higher extent than natural gas on the production processes. This is demonstrated in Table 5-VI, where a difference of 35% in the natural gas consumption is observed, 54% for the electricity and 20% for the cooling water consumption. The same conclusions are drawn in the case of the best environmental impact solutions. The respective differences are 69% for the natural gas, 34% for electricity and 25% for water.

Table 5-VI : Consumption of electricity, cooling water and natural gas as external supply for optimal solutions (operating cost and environmental impact) for scenarios S1 and S6.

	Energy requirement	Natural gas [kg]	Electricity [kWh]	Cooling water [m3]
Optimal cost solution	Real	52497	85784	284959
	Theoretical	33917	39711	225748
Optimal environmental solution	Real	108670	66654	299844
	Theoretical	33869	44034	225746

The reduction of the environmental impact up to negative values is mainly due to two effects: the reduction of natural gas consumption and the benefit of electricity selling. For the periods where the heat produced by the incineration unit is sufficient for the production processes, the decrease of the water pumping demand creates an electricity excess which is substituted 100% for the environmental impact and also reduces the operating cost but with a lower selling price compared to the electricity from the network. As the necessary heat is produced only by the incineration no additional natural gas consumption is required. Moreover, the recovery of auxiliaries (e.g., waste solvents), contributes to the negative values for the overall environmental impact relatively in a higher extent when lower energy consumption (i.e., theoretical instead of real) is assumed for the production processes. The pollutant impact does not change in a significant way indicating that the reduction of the use of steam boiler due to lower heat demand is not enough to modify this source of emissions.

From optimization point of view the use of theoretical energy requirements in simulation shows the possibility to obtain the same qualitative results in production planning and waste management as when real energy demands are considered. This allows the reduction of data collection in the first part of an energy analysis. But still final conclusions about the operating cost and the environmental impact cannot be drawn in an absolute scale.

5.4 Conclusions

In this chapter the system boundaries of the investigated integration problem were extended to include the energy utility generation system. Furthermore, heat integration based on pinch technology was added to the optimisation of production planning and waste management. This resulted in a high-level design problem (i.e., as opposed to lower level design decisions associated with scheduling tasks, dynamic operation and control of batch processes, etc.) for advanced integration of production processes, waste treatment and utility generation. The problem was formulated for the same industrial facility presented in Chapters 3 and 4.

An optimisation procedure was defined in a “sequential” approach by decomposing the overall design problem into a master and two slave problems. The design problem was treated as a multi-period problem dealing with the production planning of several batch processes (master problem), where for each period two independent slave problems are solved, that is an optimal waste mixing is determined and heat integration between all hot and cold streams of the production and waste treatment processes is performed. Additionally, the optimisation problem can be characterized as multi-objective considering both operation cost and environmental impact as objective functions. The influence of several parameters affecting this multi-period, multi-objective optimisation problem was investigated, such as the number of periods, the effect of different environmental impact indicators (EI99, UBP, CED) to be used as objective functions, and the use of accurate estimations of the real energy consumption for the production processes versus the theoretical ones.

With respect to the influence of the environmental impact indicators, it was observed that similar Pareto optimal solutions are found in all scenarios, although the trade-off extents between optimal cost and environmental performance is different for each indicator (i.e., ranging from 15%(EI99)-55%(UBP) in operating cost improvement and 1%(UBP)-60%(EI99) in environmental impact improvement along the Pareto front, respectively). Despite the differences in the environmental impact indicator concepts, they are all highly sensitive to the resource depletion impact category related with the direct and indirect energy use. Since the focus of the integration in this study is also in a big extent energy use oriented (i.e., including detailed heat integration and very limited mass integration, considering mainly waste-to-energy treatment options and energy demands from the production processes), this explains the similarity of the Pareto-optimal solutions. Therefore, an interesting conclusion is that similar future studies with emphasis on energy use could consider, for example, the less data intensive CED indicator as optimisation objective for an initial screening of high-level design decisions, without significant loss optimality in more holistic environmental impact indicators, such as the EI99.

With respect to the influence of the number of periods, a higher production planning flexibility (i.e. more production periods) allows generally for more feasible solutions and in this example also for more Pareto optimal solutions. In the cases investigated here, the optimal operation cost and environmental impact solutions found for lower number of periods are also the anchor points of the Pareto fronts for higher number of periods, showing that the integrated system is not locally sensitive to this production planning parameter. However, no conclusions should be drawn for the global sensitivity (i.e., as the number of production planning periods is significantly increased) of this or similar integrated systems. Computation time problems did not allow further investigation of the influence of the number of periods.

With respect to the influence of more accurate estimations for the energy demand of production processes (e.g., through detailed modelling of energy losses as presented in Chapter 3) versus theoretical energy demand, a different pattern has been observed with respect to the performance domain of feasible solutions, without however affecting the Pareto-front solutions. This can be considered as an indication for using the less data intensive theoretical energy demand in a first screening to eliminate a large number of feasible solutions and switch to real energy consumptions, mainly to study more accurately the Pareto optimal ones. However, the different pattern of the feasible solutions may indicate that in other cases, the Pareto-front could also be affected, and therefore, more studies are needed to support this conclusion.

Finally, it should also be mentioned that the analysis of the optimisation results, and especially the decomposition of the operation costs and environmental impacts in various categories, has provided important insights for the design of the system (e.g., the cost-environmental impact trade-offs with respect to the use of excess natural gas, the interdependencies between energy demand as a result of the production planning, incineration capacity and use of wet air oxidation, etc.) which were not straightforward to infer on the basis of empirical knowledge. This shows the importance of systematic methods to deal with complicated systems to go beyond the “low-hanging fruits” in optimisation potential.

Chapter 6

6 Summary and outlook

6.1 Summary

This thesis presents an approach with the analysis of the energy consumption in chemical batch plants, including the waste treatment and the utility generation operations. It represents a step towards advanced integration (i.e., by significantly enlarging the system boundaries) for improved plant operation from economic and environmental point of view..

In a first aspect, the energy consumption at unit operation level was studied in detail, modelling also the thermal losses calculated from the difference between the real energy consumption and the theoretical energy demand. The theoretical energy demand was defined based on a detailed energy balance of each unit operation using dynamic plant data. Thermal losses were determined using an empirical parametric equation previously developed for steam consumption in chemical reactors and applied to several equipment types and energy utilities. Thermal losses in the range of 30-50% have been identified depending on the type of energy utility. Two batch production buildings were analyzed with this method and a bottom-up model of the utility consumptions was built for both theoretical and real energy demand allowing the comparison with the measured consumption of the production building over several weeks. These examples have demonstrated the possibility to monitor the utilities consumption of the production buildings with a good accuracy (average relative error of 20%).

Moreover, several methods to estimate the real energy consumption have been assessed based on valve openings regulating utility flows. This method offers some interesting possibilities in buildings where few measurement devices are available especially on utility networks. Additionally, the method can be used for a first screening and allocation of the major influencing energy consumption processes in a chemical batch production building. In this case, the dynamic plant data will be replaced by averaged time profiles of the most important production steps. The relative error in the estimation of the method with averaged time profiles depends, of course, on the resolution of the production steps, but is not expected to deteriorate to errors higher than 30%, which is still considered satisfactory for basic design calculations, when put into perspective with the accuracy of the other metrics in the objective functions (e.g., cost factors, environmental impacts, etc.)

The second step integrates the waste management in the analysis of the energy consumption, and it does so from a life cycle perspective. A superstructure describing typical waste treatment option of a chemical site was generated with models of industrial waste treatment units. The selected waste treatment models were developed in the framework of life cycle assessment ensuring the same level of details and a complete list of material and energy consumption and pollutants emissions. Moreover, operating constraints were added to the superstructure to represent both legal and treatment limitations. Several case studies were carried within the superstructure using multi-objective optimisation to define the most promising waste mixing according to several optimisation parameters.

A first set of optimisation scenarios analysed the influence of the waste mixing policy and the choice of distillation models for solvent recovery on the treatment of a small set of waste streams, representing an annually averaged operation of a real waste treatment plant (CIMO, Monthey). It was shown that the mixing policy was observed as a key factor in the improvement of the waste management while the type of distillation models choice affects the selection of solvents to recycle.

The second set of optimisation scenarios focused on the multi-period potential of the waste management, namely the synergetic effects between a synchronized design and operation of the batch production and the waste treatment plant. Generation and treatment of particular sets of waste streams in the same production periods showed benefits in both environmental and economic indicators. The main reason is the possibility to use characteristics of some waste streams to reduce the negative impacts produced by the treatment of others. This matching of streams having mutual benefit is allowed by the multi-period system which isolates the best scenarios. If this synergetic benefit is not realized in the same period, it could be still realized with additional waste storage tanks and appropriate storage policies, which however have an economic downside in the capital investment cost. This scenario has not been considered in the present study.

The last step integrates in a common framework the production energy requirements, the waste management and the design of the energy utilities generation system. The previous superstructure was extended to include utility production units and utility networks were built between all units to obtain an optimal integration effect. An optimisation procedure was defined to split the global problem into one master problem and two independent slave problems solved in a hierarchical way. This formulation was a consequence of the choice of the computational environment (i.e., modelling platform and available optimisation solvers). Several multi-objective, multi-period optimisation scenarios were carried out to analyse the effect of the environmental indicator choice on the Pareto-optimal solutions. The number of periods and the description of the energy requirements for the production processes were investigated too. The results demonstrated that different environmental impact indicators lead to similar Pareto-optimal solutions, which are also not locally sensitive to the number of periods. Moreover, the more accurate estimation of the energy demand of the production processes (i.e., real versus theoretical energy demand) does not seem to have a significant effect on the Pareto front.

6.2 Outlook

This thesis provides models and optimisation procedures for advanced integration of batch plants with waste management and energy utility production systems. It also provides opportunities for further development and/or refining of developed models and optimisation procedures in the direction of representing more accurately the complicated industrial systems and including additional components and plant configurations. An overview of these opportunities is presented in the next paragraphs.

The validation of the thermal losses model for water consumption in Chapter 3 can be extended to other cooling fluids, such as brine. Larger thermal losses can be expected for this type of utility because of the larger temperature difference to the ambience. Moreover, the brine network is not constantly recirculating the cooling medium, especially in the last sections of the pipes between the units using brine and the main pipes of the brine network.

Significant effort would be required to extend the present energy consumption models for electricity consumption. A first approach using the nominal power of electrical motors and some estimations of the efficiency of electrical conversion according to several process parameters can be made to obtain an overview of the overall energy efficiency in the batch production building. However, monitoring of the electricity consumption based on process data, like in the case of steam and cooling water, is more challenging because the necessary process data to calculate the power requirements can not be easily obtained, especially in the case of large multiproduct/multipurpose batch production buildings.

More potential for further work present the waste treatment processes and waste management concepts of Chapter 4. Each waste treatment process is typically designed and optimized for a particular kind of waste streams, relevant to the industrial facility that it serves. The present study used an LCIA waste treatment model developed for a different industrial facility and therefore, it would be interesting to update the model and observe the impact on the optimisation results. Creating a database of LCIA waste treatment models for different plant specifications throughout a region (e.g., Switzerland) can lead to an extension of the waste mixing problem to a country wide scale. This will consider new constraints due to waste transportation, for example, but will also provide more potential for optimized waste management scenarios towards an “industrial symbiosis” approach in the domain of waste management.

Another extension of the present work refers to dynamic features of the waste management problem (i.e., lower level design). To this end, it can be investigated how easy a detailed scheduling of available waste storage and mixing can realize the high level design targets of production planning and waste management presented in this work. In this case, considering the possibility of waste storage in the waste management should also be included in the high-level design problem. Storage can generally add significant flexibility in multi-period problems for batch operations. Other constraints, like piping or generally waste transportation restrictions, safety constraints, more detailed waste mixing restrictions, random events in production calling for re-planning, can be considered to address the issue of the flexibility of the generated designs and simulate more closely the industrial reality.

To this end, also LCIA oriented modelling of various pretreatment operations (e.g., mechanical separations, precipitations, pH adjustments, etc.) performed on waste streams before sending to the final waste treatment processes can enhance the waste treatment models used in this thesis. Integration of these operations in the system can offer new possibilities to assess the necessity of those pretreatments or the degree of purification needed before final treatments.

More environmental impact indicators can also be used in the assessment of the optimisation scenarios of Chapters 4 and 5, to show in what extent these can affect the obtained solutions. As environmental impact indicators are often aggregations of several sub-indicators, the comparison and the identification of the components or the utilities which are responsible of the differences can simplify the LCIA process by reducing the data collection to a small number of elements which have significant impacts.

Regarding the heat integration procedures, the production planning can be defined in a more detailed way allowing the heat integration between production process streams. Moreover, energy storage policies can be included to increase the heat recovery in the same period or between periods. Another possible way to reduce utilities consumption is to study possible reuse of water or condensate of steam. Depending on the output temperature, cooling water can be further used in additional units requiring cooling at higher temperature. In some cases, it is also possible to reuse the condensate to preheat process streams. Furthermore, a more accurate cost estimation, the design of heat exchanger network can be included to define the investment cost of the equipment and to consider the whole cost of the heat integration. Finally, the heat integration approaches can be significantly enhanced with mass integration strategies either within the plant or between different plants in the proximity, in a source-sink approach minimizing the waste loads for the waste treatment operations.

7 List of symbols

SYMBOLS

a	Heat loss coefficients	[kJ^{1-b}]
b	Heat loss coefficients	[-]
c	Concentration	[g/l]
cf	cost factor	[MU/kg], [MU/kJ]
c_p	Heat capacity	[kJ/(kg K)]
d	Period duration	[week]
ef	Environmental factor	[pts/kg], [pts/kJ]
k	Heat loss term	[kW/(m^2 K)]
lb	Lower boundaries	[-]
m	Mass	[kg]
n_q	Number of temperature intervals	[-]
q	Flowrate of waste stream	[kg/h], [m^3/h]
r	reaction rate	[kg/min]
t	time interval	[min]
ub	Upper boundaries	[-]
x_1	Maximal flow through a valve	[m^3/h]
x_2, x_3	Fitting parameters	[-]
y	Binary variable for process activity	[-]
A	Surface	[m^2]
BC	Base consumption of the building	[to/h]
E	Energy flow	[kW]
E^{UO}	Energy of unit operation	[kJ]
H	Total time for production planning	[week]
Kvs	Flow factor	[m^3/h]
MU	Monetary unit	[-]

OF	Objective function	[-]
PP	Process production in horizon H	[kg]
Q	Flowrate	[kg/h], [m^3/h]
QE	Pollutant flowrate	[kg/h]
QU	Utility or auxiliaries flowrate consumption	[kg/h], [kW]
R	Residual energy after heat recovery	[kJ]
T	Temperature	[K]
T*	Corrected temperature with $\Delta T_{min/2}$	[K]
VO	Valve opening	[-]
α	Set of streams	[-]
$\Delta_r H$	Reaction enthalpy	[kJ/kg]
$\Delta_{vap} H$	Evaporation enthalpy	[kJ/kg]
$\Delta_c H$	Combustion enthalpy	[kJ/kg]

INDICES

amb	Ambient
av	Average
cold	Cold
cu	Cold utility
Diss	Mechanical energy transformed into heat
equip	Equipment
evap	Evaporation
hot	Hot
hu	Hot utility
H/Csys	Heat/cooling system
max	Maximum
min	Minimum
Meas	Measured
Loss	Thermal losses
prod	Chemicals in reaction mass
Theo	Theoretical

util	Utility
h	Chemical process
i	Waste stream
j	Component of waste stream
k	Waste treatment
l	Input constraint for waste treatment
m	Utility or auxiliary
n	Pollutant
p	Production period
q	Temperature interval
r	Hot stream
s	Cold stream
t	Time t
u	Utility generation unit
v	Control valve

8 Appendices

A. Bottom-up modeling for monoproduct building

Figures A1 and A2 present the steam consumption in the monoproduct building for the two products produced by batch process 1.1 (see Figure 3-1) in a single campaign mode. The water consumption for the same products is presented in Figures A3 and A4 respectively. The base consumption for both kinds of utilities was measured during production shutdown in the monoproduct building during summer and winter for the first and the second product, respectively. As expected, because of the smaller complexity of the monoproduct compared to the multiproduct building, for both energy utility consumptions the bottom-up model estimations are matching better with the building measurements.

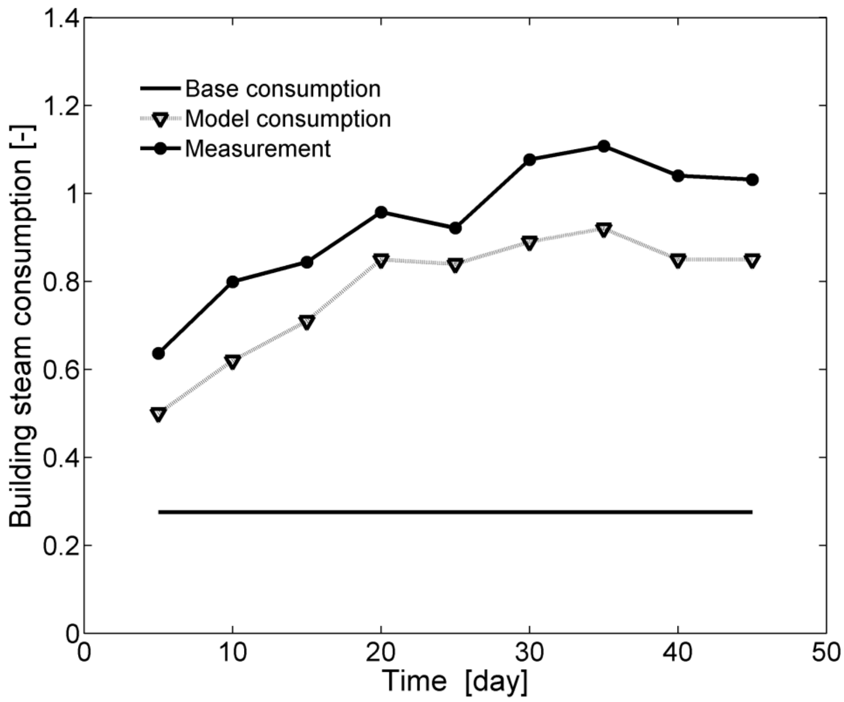

Figure 8-1 : Bottom-up modeling for steam consumption in the monoproduct building for the first product produced by batch process 1.1 (Figure 3-1). Modeling is performed on 5-days aggregation basis. The values are given in relative terms using as reference basis the average building consumption over a 5-days period of normal operation. The base consumption was measured during a shutdown of production in winter, where this product is produced. The relative average modeling error at building level is 17%.

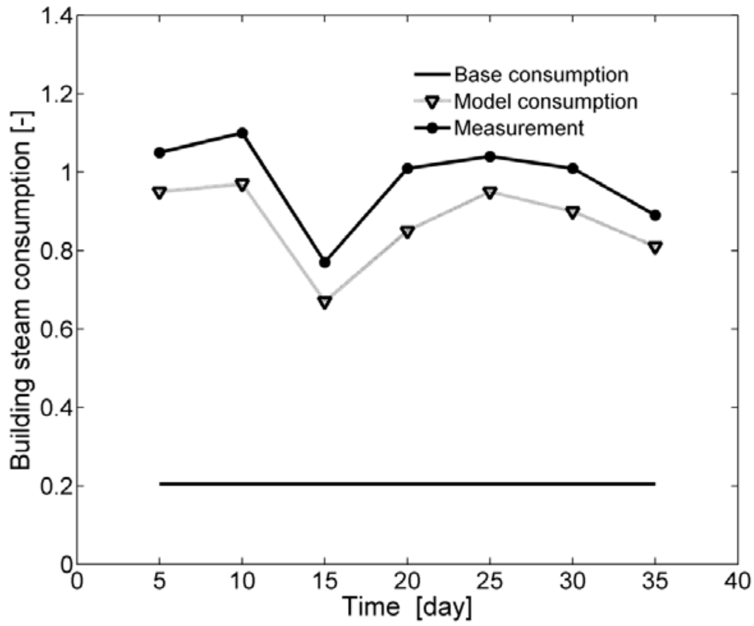

Figure 8-2 : Bottom-up modeling for steam consumption in the monoproduct building for the second product produced by batch process 1.1 (Figure 3-1). Modeling is performed on 5-days aggregation basis. The values are given in relative terms using as reference basis the average building consumption over a 5-days period of normal operation. The base consumption was measured during a shutdown of production in summer, where this product is produced. The relative average modeling error at building level is 11%.

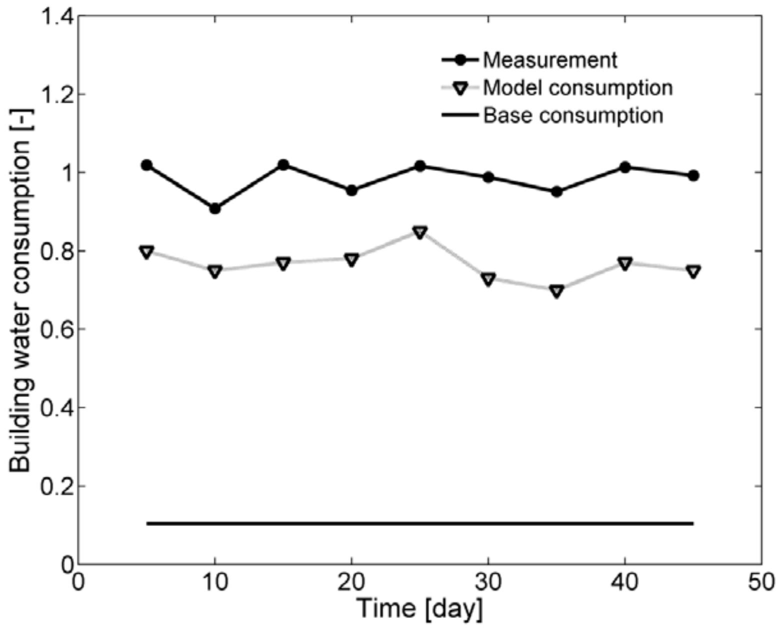

Figure 8-3 : Bottom-up modeling for cooling water consumption in the monoproduct building for the first product produced by batch process 1.1 (Figure 3-1). Modeling is performed on 5-days aggregation basis. The values are given in relative terms using as reference basis the average building consumption over a 5-days period of normal operation. The base consumption was measured during a shutdown of production in winter, where this product is produced. The relative average modeling error at building level is 23%.

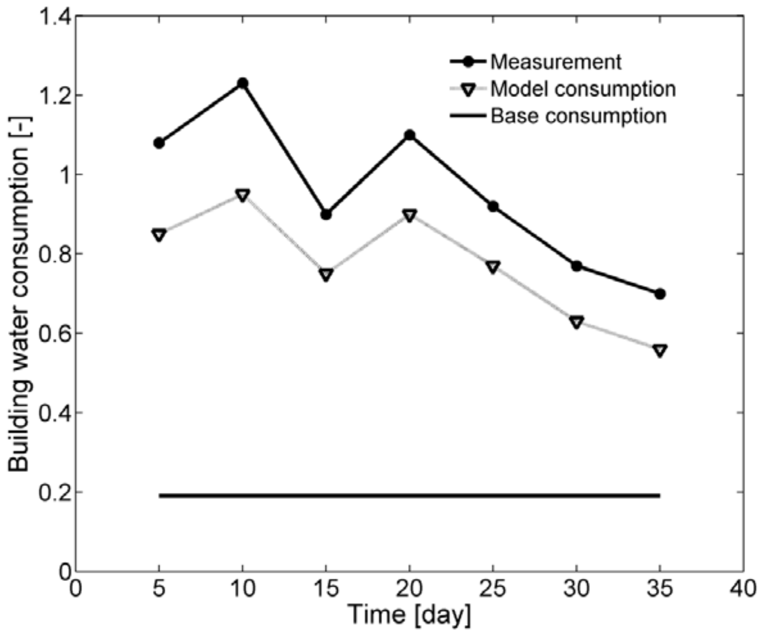

Figure 8-4 : Bottom-up modeling for cooling water consumption in the monoproduct building for the second product produced by batch process 1.1 (Figure 3-1). Modeling is performed on 5-days aggregation basis. The values are given in relative terms using as reference basis the average building consumption over a 5-days period of normal operation. The base consumption was measured during a shutdown of production in summer, where this product is produced. The relative average modeling error at building level is 20%.

Brine is also used for cooling purposes in the monoproduct building but its production is performed inside the building and therefore an overall building flowmeter for brine was not available. Moreover, an allocation of the electricity and cooling water consumption used for brine production was not possible, and for this reason the modeling results for brine consumption could not be validated and are not presented here.

B. Top-down approach

A different approach for energy modeling is the top-down approach that correlates productivity data with energy utility consumption (Bieler et al., 2003). This approach was also tested in the case of the monoproduct building (Figure A5), but the variability of the productivity was not sufficient to develop accurate correlations for the energy consumption. In the case of steam some correlation was detected, which by extrapolation could also estimate sufficiently well the base steam consumption of the building. However, for cooling water such a correlation could not be detected. Since previous studies have already demonstrated that the top-down approach has severe shortcomings when applied to more complicated production buildings, it was not applied to the multiproduct building of the case study plant.

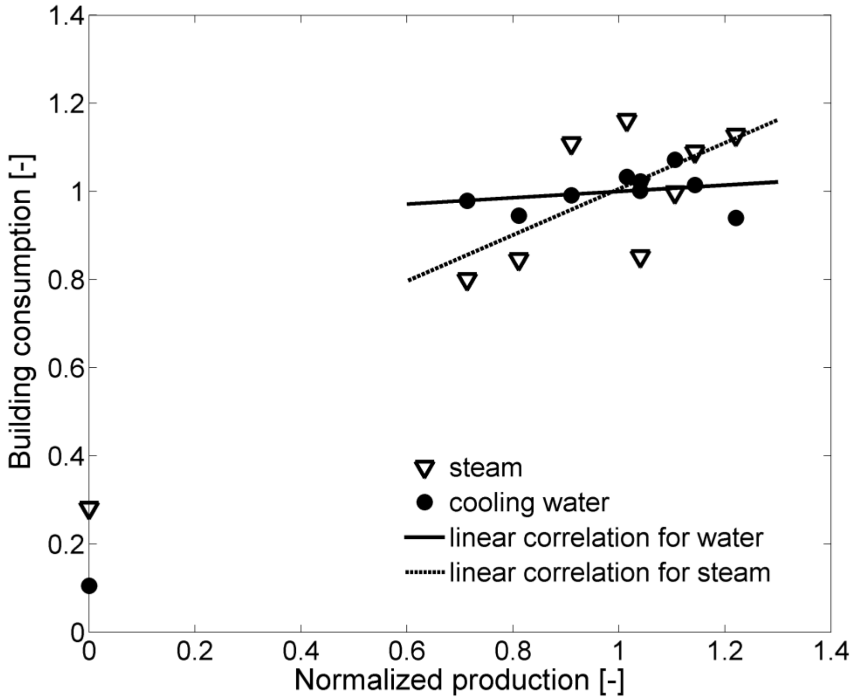

Figure 8-5 : Top-down approach for steam and cooling water consumption in the monoproduct building for the second product produced by batch process 1.1 (Figure 3-1). Aggregation is performed on weekly basis and the values are given in relative terms using as reference basis the average building production and energy consumption over the whole period. The lines refer to linear regression using only data during production.

C. Thermal losses coefficients for condensers and heat exchangers

In the case of heat exchangers and condensers, a modification of eq 3.8 is used to fit the thermal losses coefficients. As mainly heat exchangers do not have a heating/cooling system comparable to this of reactors, the first part of eq 3.8 is omitted resulting in eq 8.1:

$$E^{UO}_{Loss,t} = E^{UO}_{Util,t} - E^{UO}_{Theo,t} = \pm k \cdot A \cdot (T_{Util,t} - T_{amb}) \cdot \Delta t \qquad 8.1$$

The sign is positive for heating and negative for cooling operations. An additional modification is made about the reference temperature, where the utility input temperature ($T_{Util,t}$) is used instead of the reaction mass temperature ($T_{prod,t}$).

D. Influence of pressure drop on flow rate

The steam flow rate through a control valve depends on equipment specification and operational conditions. As steam is a compressible fluid, pressure plays an important role in the flow rate regulation.

A complete formulation of the turbulent flow rate of a compressible fluid through a control valve is given by

$$Q = C \cdot N \cdot F_p \cdot \left(1 - \frac{x}{3 \cdot x_{chocked}}\right) \cdot \sqrt{x \cdot p_1 \cdot \rho_1} \qquad 8.2$$

$$x = \frac{p_1 - p_2}{p_1} \qquad 8.3$$

where p_1 is the valve input pressure, p_2 is the valve output pressure, C is a flow coefficient as a function of the valve opening, N is a numerical constant, F_p is a piping geometry factor, ρ_1 is the density of the fluid at the input, $x_{chocked}$ is an intrinsic valve characteristic referring to the maximum possible value of x, and Q is the steam flow rate. Assuming that p_1 is constant and equal to the steam pressure provided by the steam generation and distribution system (e.g., 6-bar steam), only two of these parameters are changing with the valve opening: parameter C depending on the geometry of the free space regulated by the valve for the steam flow, and parameter x depending on the heat exchange conditions in the equipment after the valve. The influence of x is expressed by the last two factors in eq 8.2 and will be referred as correction factor for the flow inferred only based on C. On the other hand, if p_2 is measured (or the respective temperature assuming that it refers to saturated steam), then an exact calculation of this correction factor would be possible. Unfortunately, in this case study there were no available measurements in the electronic registration system for the respective pressures or temperatures after the valves, and only mechanical pressure sensors (i.e., measurement taken by visual inspection) were available making impossible the recording of pressure data in high resolution (see also Figure 8-6).

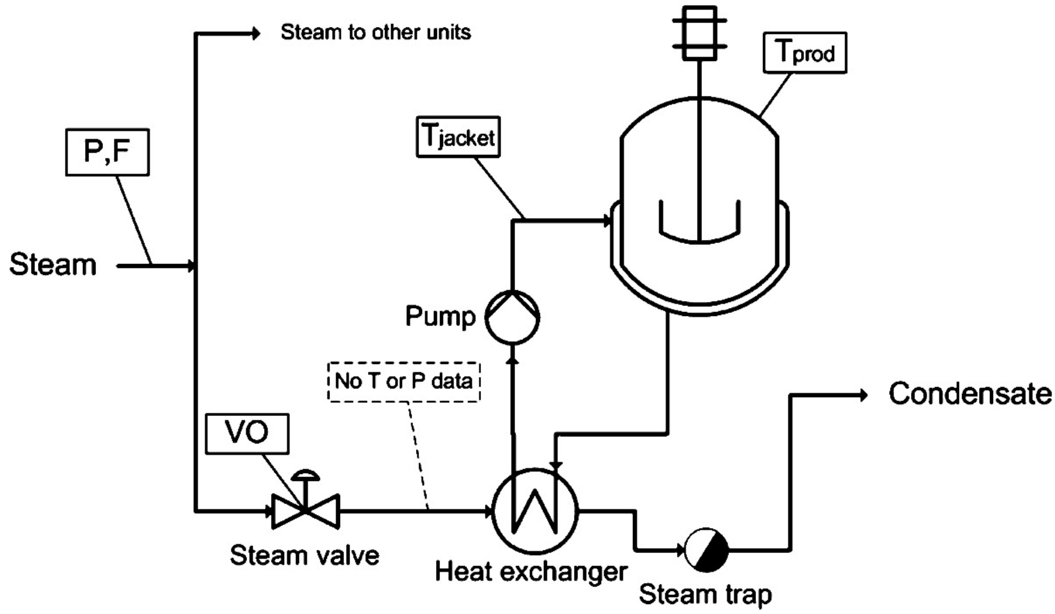

Figure 8-6 : Typical configuration of a steam heating system for a batch reactor in the multiproduct plant of the case study. No pressure or temperature sensor is available after the valve for electronic data registration (only mechanical sensors available). P, pressure; F, flow; T, temperature; VO, valve opening.

According to good practice in valve design (Spirax-Sarco, 2007), parameter x has to be in a range from 0.1 to 0.6 to ensure optimal conditions for flow control and typical values of xchocked range between 0.4 and 0.8. Using eqs 8.2-8.3, it is possible to define the deviations due to pressure drop difference in the steam flow derived by the valve opening calibration curves (see Table A1). For instance, according to Table A1, a correction factor of 0.456 corresponds to a valve with intrinsic characteristic value of $x_{chocked}$ = 0.6 operating under conditions where x = 0.3. This correction factor represents the pressure drop dependent factors of eq 8.2 and therefore remains constant for unit operations stipulating similar pressure drops. Thus, when valve calibration is performed under operating conditions, this correction factor is integrated in the calibration curve, and only deviations from this pressure drop are relevant. In multiproduct batch plants with dedicated production lines, it is safe to assume that a given piece of equipment performs similar unit operations and therefore only small deviations in x are expected, for example, $\Delta x_{max} = 0.1$. Then, from Table A1, it is easy to calculate an overall average relative error (12%) for the steam flow estimation when only the valve opening calibration curve is used. In fact, if the operating conditions impose a range for x between 0.2–0.6, then this average relative error is further reduced to 7%.

Table 8-I : Correction factors for considering the impact of pressure drop (x) across control valves according to eqs 10 and 11[a]

	$x_{chocked}$				
x	0.4	0.5	0.6	0.7	0.8
0.1	0.290	0.295	0.299	0.301	0.303
0.2	0.373	0.388	0.398	0.405	0.410
0.3	0.411	0.438	0.456	0.469	0.479
0.4	0.422	0.464	0.492	0.512	0.527
0.5	0.422	0.471	0.511	0.539	0.560
0.6	0.422	0.471	0.516	0.553	0.581

[a]The valve inlet conditions refer to 6-bar steam.

Small values of x are generally expected when valves are almost fully open, e.g., at more than 80% valve opening. As it can be seen in Table A2, a very small percentage of valves was operating with valve openings more than 80% in the investigated period, and therefore, the lower estimation (to 7%) applies for the results of this study (i.e., additional relative errors closer to 7% should be expected by neglecting the pressure drop in the steam flow calculation).

Table 8-II : Distribution of valve openings (VO) for all open control valves in the Case Study plant during the investigated period[a]

	Valve opening				
valve	0 < VO < 20	20 < VO < 40	40 < VO < 60	60 < VO < 80	80 < VO <100
1	1.00	0.00	0.00	0.00	0.00
2	0.95	0.05	0.00	0.00	0.00
3	0.66	0.34	0.00	0.00	0.00
4	0.93	0.03	0.01	0.03	0.01
5	0.89	0.05	0.06	0.01	0.00
6	0.82	0.04	0.11	0.02	0.01
7	1.00	0.00	0.00	0.00	0.00
8	0.98	0.01	0.01	0.00	0.00
9	0.98	0.02	0.00	0.00	0.00
10	1.00	0.00	0.00	0.00	0.00
11	0.52	0.48	0.00	0.00	0.00
12	1.00	0.00	0.00	0.00	0.00
13	0.68	0.32	0.00	0.00	0.00
14	0.65	0.00	0.35	0.00	0.00
16	1.00	0.00	0.00	0.00	0.00
17	0.46	0.01	0.00	0.00	0.53
18	0.46	0.54	0.00	0.00	0.00

[a]Most of the control valves are not fully open (i.e., more than 80%) for long time periods, decreasing the chances for very low values of pressure drops and therefore of x with respect to Table 8-I.

E. Outline of a first-principles approach for steam flow calculation

The calculation of steam flow can be based on theoretical energy demand and heat transfer principles including estimation of steam pressure on the utility side of the heat exchanger. However, an additional assumption for heat losses is necessary or a detailed and complicated analytical calculation for all components of the heating/cooling utility system. If, for instance, thermal losses are 40% of the theoretical energy demand, then

$$P_{Theo} + P_{Loss} = U \cdot A \cdot (T_{steam} - T_{prod}) = Q_{steam} \cdot \Delta_{vap}H \qquad 8.4$$

where P_{Theo} and P_{Loss} are the heat transfer rates for theoretical consumption and heat transfer losses respectively, U is the overall heat transfer coefficient, A is the heat transfer area, T_{steam} and T_{prod} are the temperatures on the two sides of the heat exchanger, Q_{steam} is the steam flow rate, and $\Delta_{vap}H$ is its latent heat.

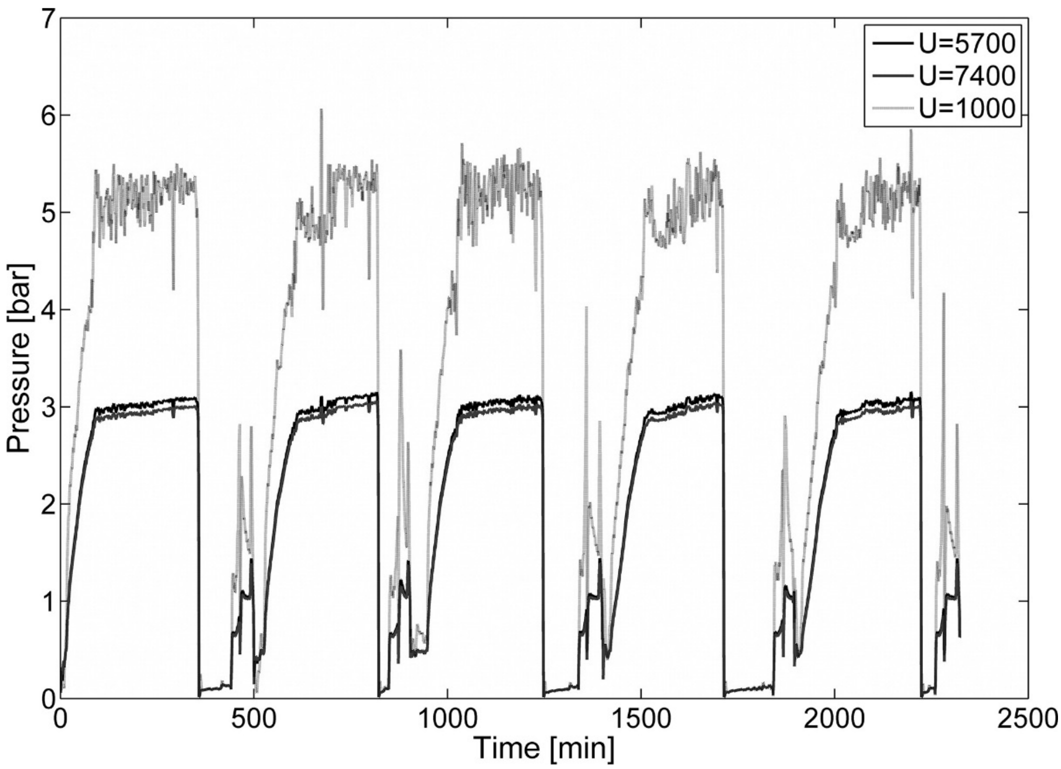

Figure 8-7 : Steam pressure profile on utility side of heat exchanger for 5 batches performed in a 10 m^3 reactor used for heating and batch distillation purposes. The profiles are determined according to eq 8.4 based on the theoretical energy demand of the process steps in the reactor, and assuming heat transfer losses (40% of the theoretical energy consumption), typical heat transfer coefficients (U [W/(m^2 K)]) for plate heat exchangers and saturated conditions for steam at the inlet and outlet of the heat exchanger.

The detailed determination of overall heat transfer coefficient implies a large amount of information about heat exchanger structure and fluids involved in the heat transfer. Three typical values of U for plate heat exchangers are 1000, 5700, and 7400 W/(m^2 K). As A and T_{prod} are typically known, it is possible to calculate from eq 8.4 the steam temperature, the corresponding pressure assuming saturated conditions (see Figure A7), its latent heat and finally the steam flow. Figure A8 shows the different steam flows as function of the heat transfer coefficient and compares these values with the steam flow obtained by valve calibration based only on valve opening.

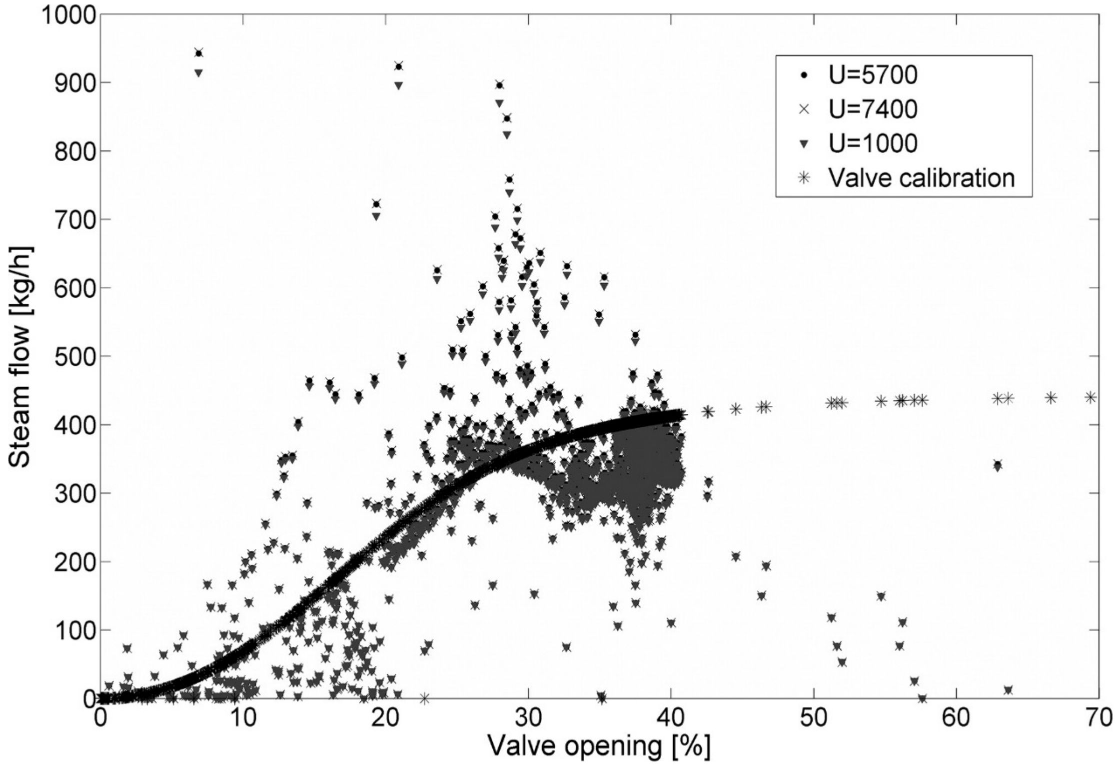

Figure 8-8 : Steam flow estimations based on eq 8.4 and pressure profiles in Figure A7 (U [W/(m^2 K)]) versus those obtained by control valve calibration.

F. Degrees of freedom for steam flow calculation, enhanced multiple nonlinear regression and "black-box" modeling

From eq 8.4, where it is assumed that heat transfer takes place only due to the latent heat of steam (i.e., that T_{steam} is fully defined by P_{steam} after the valve), and considering that U depends on T_{steam}, T_{prod}, and Q_{steam}, it can be easily derived that there are three independent parameters, that is, T_{steam}, T_{prod}, and Q_{steam} or equivalently P_{steam}, T_{prod}, and Q_{steam}. Substituting x from eq 11 to eq 10 (with $p_2 = P_{steam}$) results in one equation relating Qsteam, P_{steam}, and the valve opening (C = f(VO)). This means that if T_{prod} is known, it is possible to combine eq 8.3 and 8.4 in order to relate Q_{steam} as a nonlinear function of the valve opening (C) and T_{prod}. However, the analytical form of this nonlinear function can not be readily derived, since it would involve solving explicitly U = g(T_{steam}, T_{prod}, Q_{steam}) for Q_{steam}, which is highly nonlinear with respect to flow rates and physical property dependence on temperatures.

Instead, two different approaches were used. First, an enhanced multiple nonlinear regression was applied as in eqs 3.3–3.6, where now the steam flow of each valve is described by eq 8.3 assuming an arbitrary sigmoid nonlinear function to describe the dependence of T_{prod} on P_{steam}. Then, for each valve, the model describing the steam flow would have the following form:

$$\begin{aligned} Q_{steam} &= f_1(VO) \cdot f_2\left(T_{prod}\right) \\ &= f_1(VO) \cdot \left(c_4 \cdot \sqrt{f_3\left(c_5 \cdot T_{prod}\right)}\right) \cdot \left(1 - f_3\left(c_5 \cdot T_{prod}\right)\right) \end{aligned} \quad 8.5$$

where f_1(VO) can have the form of eq 3.1 or 3.2, and f_3(c5T) is the general sigmoid nonlinear function. In Table A3, the results of this procedure are summarized and compared with the case that only the valve opening is used to estimate the steam flow (i.e., only f_1(VO)). There, it is clear that T_{prod} does not improve the estimation of the steam flow, for two different forms of splitting between training and validation data representing a pure extrapolation case with respect to the time series (i.e., the points used for validation are subsequent in time with respect to the points used for training) and a strong interpolation case where every second data point was used for validation.

Table 8-III : Performance of multiple nonlinear regression models (MNLR) and neural networks (RBFNN) for estimating steam consumption using either only the control valve opening (VO) or the control valve opening (VO) together with the temperatures of the production process (VO–T_{prod})[a]

		training set 1	validation set 1	training set 2	validation set 2	training set 1
MNLR–VO	R^2	0.847	0.752	0.822	0.816	
	MARE	11.0	16.9	14.3	14.2	
	d1	0.831	0.739	0.803	0.801	
	d2	0.956	0.917	0.945	0.943	
MNLR–VO–T_{prod}	R^2	0.832	0.730	0.804	0.796	
	MARE	10.9	16.4	13.6	13.6	
	d1	0.825	0.741	0.804	0.802	
	d2	0.954	0.916	0.944	0.941	
RBFNN–VO	R^2	0.890	0.650	0.858	0.849	
	MARE	8.4	23.7	10.6	10.5	
	d1	0.869	0.653	0.847	0.846	
	d2	0.970	0.875	0.961	0.958	
RBFNN–VO–T_{prod}	R^2	0.900	0.603	0.889	0.883	
	MARE	7.9	25.7	8.7	8.6	
	d1	0.880	0.631	0.876	0.875	
	d2	0.973	0.849	0.970	0.968	

[a]Two different forms of splitting between training and validation data are used representing a pure extrapolation case (training and validation sets 1) with respect to the time series and a strong interpolation case (training and validation sets 2). Four different metrics are reported for assessing model performance, R^2, coefficient of determination; MARE, mean value of the absolute relative errors; d1, d2, modified metrics of R^2 type (Willmott et al., 1985).

In a second approach, a neural network was used to estimate the overall steam consumption based on the valve openings and the T_{prod} for all the production processes. The neural network had the general form of a radial-basis-function neural network (RBFNN) trained with an algorithm based on a fuzzy partition of the input space (Alexandridis et al., 2011). This type of neural network has the properties of a universal approximator, and therefore, given sufficient amount of training data, it can demonstrate excellent interpolation performance. In this method, which consists of fuzzification of the input space, clustering of the input data based on the fuzzified multidimensional grid of the input space, and multiple linear regression of the cluster membership function values for each input data point, the more important parameter that controls the RBFNN complexity is the resulting resolution of each input variable, as defined by the number of the fuzzy sets that it is divided into. A higher number of fuzzy sets will result in a higher resolution for the respective input parameter and, therefore, in a neural network that will have better accuracy and possibly worse generalization performance. Typically, this trade-off is observed by monitoring the performance on a validation set to determine the optimal value of this parameter.

The results of the RBFNN for both types of splitting between training and validation sets are also presented in Table A3 and Figure A9, which is comparable to Figure 3-2. Again, it is clear that only minor improvement is achieved by including the temperatures (T_{prod}) as additional source of information. For instance, the improvement in the average relative error is between 2% and 3%, which is even smaller than the expected value of 7% when x in eq 10 is ranging between 0.2 and 0.6, as discussed in paragraph D. Moreover, for the first splitting representing the extrapolation performance, Figure A10 shows that better results are obtained when the valve opening variables have higher resolution than the temperature variables, indicating that the variability of the valve openings is better related with the variability of the overall steam consumption of the plant.

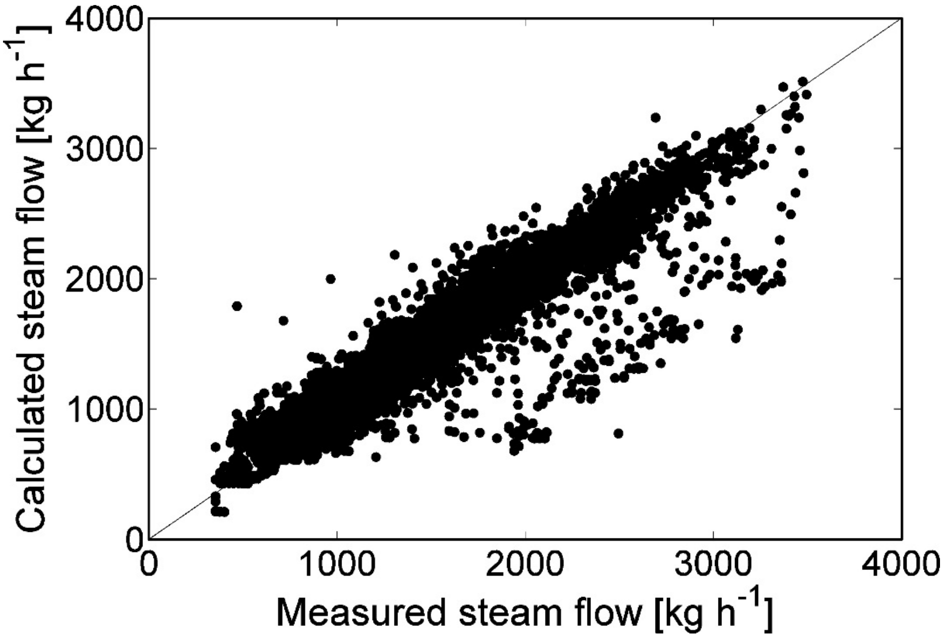

Figure 8-9 : Scatter plot of measured versus calculated flow for steam control valves using a neural network approach based on 11300 measurements (1-min time interval, R^2 = 0.89).

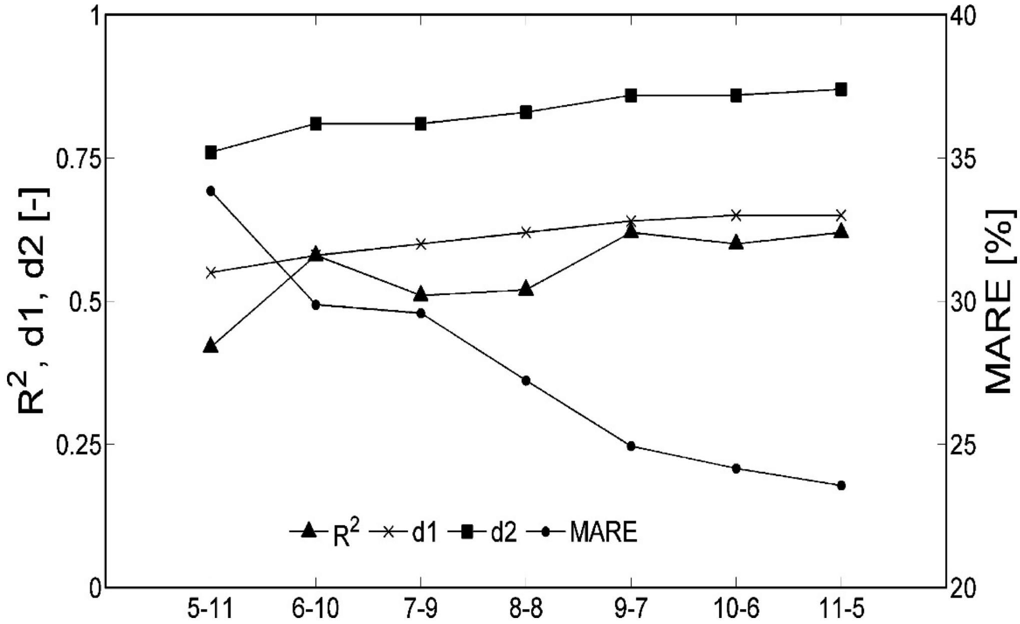

Figure 8-10 : Influence on the neural network performance of different number of fuzzy partitions between the valve openings and the temperatures of the production process (e.g., y–z denotes y-fuzzy partitions for the valve opening variables and denotes z-fuzzy partitions for the temperatures of the production process). Four different metrics are reported for assessing model performance: R^2, coefficient of determination; MARE, mean value of the absolute relative errors; d1 and d2, modified metrics of R2 type (Willmott et al., 1985).

G: Environmental impact and operating cost factors

Table 8-IV : Environmental impact according to Eco-indicator 99(H,A) methodology for pollutants described in LCIA models (Source: Ecoinvent database). The symbol — indicates that the respective data is not available

Resource	Price [MU/kg]	Impact [pts/kg]	Remark
CO_2	5.50e-3	-	
CO	8.40e-3	-	
NMVOC	3.32e-2	-	
NOx	2.75	-	
Particule	9.74	-	Particule + P_2O_5
SO_2	1.50	-	
NH_3	3.42	-	
HCl	5.50e-3	-	HCl + HBr + HI
HF	0	-	
Fe	0	0	
Co	0	0	
Ni	554.72	11.15	
Cu	113.84	11.46	
Zn	225.34	1.27	
Cl, Br, F, I	-	0	as Cl^-, Br^-, F^-, I^-
Na	-	0	as Na^+
SO_4^{2-}	-	0	
PO_4^{3-}	-	0	

Table 8-V : Environmental impact according to Eco-indicator 99(H,A) methodology and price for energy utilities and chemical auxiliaries described in LCIA models. Prices are given in arbitrary monetary units (source for environmental impact: Ecoinvent database; source for prices: industrial partners). The symbol — indicates that the respective data is not available

Resource	Price [MU/kg]	Impact [pts/kg]	Remark
steam	5.60e-2	1.59e-2	6 bar
electricity	0.09	4.30e-3	MU/kWh
natural gas	0.60	4.00e-3	MU/MJ
NaOH 30%	0.57	5.12e-2	
HCl 32%	0.19	5.09e-2	
NH_4OH 25%	0.25	6.27e-2	as liquid ammonia
deionized water	1.50e-3	4.02e-5	
river water	1.50e-4	-	
$CaCl_2$ 77%	0.77	4.88e-2	
TMT 15	0.44	0.22	as organic chemical
Polyelectrolyte	0.44	0.22	as organic chemical
$FeCl_3$ 40%	0.36	5.14e-2	
H_2SO_4 96%	0.09	3.72e-2	
HNO_3 50%	0.22	9.62e-2	
NaOCl 40%	0.20	5.00e-2	
NaHS	1.78	3.86e-2	as inorganic chemical
activated coal	1.60	0.34	
lubricating oil	-	0.28	
CaO	0.14	2.68e-2	
Flocculant	0.44	0.22	as organic chemical
P precipitant	0.36	3.86e-2	as inorganic chemical
antifoaming	1.00	0.22	as organic chemical

Table 8-VI : Environmental impact according to Eco-indicator 99(H,A) methodology and price for waste treatment and final disposal processes described in LCIA models. Prices are given in arbitrary monetary units (source for environmental impact: Ecoinvent database, source for prices: industrial partners; TC: included in the respective waste treatment cost; M: calculated according to the LCIA models). For the final disposal treatment processes, the origin of the respective waste flows is given in parenthesis according to Figure 4-1 (DIST: distillation, INC: incineration, WAO: wet air oxidation, WWTP: wastewater treatment plant)

Resource	Price [MU/kg]	Impact [pts/kg]
Landfill disposal for metal sludge	-	2.59e-2
Incineration of metal sludge	-	1.11e-1
Municipal sewage treatment	-	4.2 1e-2
Municipal incineration	-	1.11e-1
Hazardous incineration	2.00e-1	-
Wet air oxidation	2.10e-1	-
Industrial sewage treatment	3.00e-3	-

H: Operating constraints for WWTP and WAO

Table 8-VII : Values for operating constraints used in WWTP and WAO (source: industrial partners)

Substance	Value	Unit	Treatment
TOC	<30	g/l	WAO
salt	<13	g/l	WAO
Cl + Br	<5	g/l	WAO
F	<5	ppm	WAO
I	<5	ppm	WAO
P	<20	g/l	WAO
Ca	<100	ppm	WAO
Mg	<100	ppm	WAO
BOD/TOC	>1.5	-	WWTP
salt	<10	g/l	WWTP
sulfate	<0.3	g/l	WWTP
TOC	<1.8	g/l	WWTP
PO_4^{3-}	<0.01	g/l	WWTP
P	<0.015	g/l	WWTP
N	<0.07	g/l	WWTP

Table 8-VIII : Bacteria toxicity defined as half maximal inhibitory concentration (EC50) for the marine bacteria Vibrio fischeri. Missing data are completed with the respective value for microorganism toxicity from safety data sheet. (References: 1, Handbook of Environmental Data on Organic Chemicals, 4th ed., Wiley, 2001; 2, K.L.E. Kaiser and V.S. Palabrica, 1991, Water Pollut. Res. J. Can., 26(3): 361–431; 3, BASF, MSDS Sheet, Toxicity to Microorganism.)

Chemical	EC50 [mg/l]	Reference
Ethanol	36,000	1
Methanol	105,000	1
Toluene	20	1
n-Butyl acetate	70	2
1,2-Ethanediol	110,000	1
4-Methylpentan-2-one	80	1
N,N-Dimethylmethanamide	20,000	1
Formaldehyde	92	1
Formic acid	47	3
Formamide	10,000	3
1,2-Pentanediol	10,000	3
1,2-Propanediol	26,800	1

I: Scenarios 2 and 3 of Case Study 1 (CS1)

Figure 8-11 presents the optimization results for scenario 2 of CS1, where one of the distillation columns operates in continuous mode with better recovery and reduction in utility consumption, according to the industrial LCIA models (Capello et al., 2005). Therefore, better performance in both objectives is observed as expected in this scenario (see also Figure 4-2 of the main text for comparison). Moreover, from the respective mixing description of the groups of solution given in Table 8-IX. Certain similarities are obvious with the solutions of scenarios 1 of CS1 (see also Table 4-III of the main text for comparison). For instance, regarding the Pareto front solutions of groups H and F, their mixing pattern is qualitatively almost identical to the one of the Pareto front solutions of groups J and F in scenario 1 of CS1. The only difference lies in their performance, since the increase of solvent recovery from 80% to 90% reduces the environmental impact by 6% and the operating cost by 4%. Other general similarities between scenarios 1 and 2 of CS1 refer to the steep Pareto front with respect to the environmental objective, the best economic performance achieved by recovering of the solvents in stream 3 rather than stream 4, and the general improvement of solutions when solvents from two streams are recovered instead of one.

Figure 8-12 presents the optimization results for scenario 3 of CS1, where the difficulty of azeotropic distillation is considered by using the maximal values from the respective utility consumption and emission distributions of the LCIA batch distillation models. This is done to investigate the sensitivity of the results regarding the treatment of stream 3 in a distillation column, which is not performed in the industrial practice because the solvent mixture forms a homogenous azeotrope. The respective mixing description of the groups of solutions is given in Table 8-X. The main feature of the optimization results for this scenario is the absence of Pareto front solutions including stream 3 for distillation. This result in a rather small difference between the best cost solution and the best environmental solution, i.e., groups F and G differ only in the amount of waste sent to WAO and not in the solvents to be recovered by distillation. Apart from this, they are very similar solutions to the best environmental solution of scenario 1 (group J, see also Figure 4-3 of the main text). On the other hand, group F representing the optimal cost solution in scenarios 1 and 2 corresponds now to group D, which is dominated by groups F and G of scenario 3 due to the higher utility consumption imposed by considering the azeotrope.

Scenarios 2 and 3 show that the optimization of the industrial system can be sensitive to the operating mode of the distillation units used for recovery and to the distillation conditions depending on the difficulty of the recovery task. In this case study, while considering continuous distillation generally improves the performance without significantly distorting the pattern of solutions, the implications of azeotropic distillation may be significant for the pattern of the Pareto front.

Table 8-IX : Optimization results for scenario 2 of CS1 (five waste streams S1-S5 [Table 4-I], one continuous and one batch distillation column, no consideration of azeotropes). BC indicates the base case with limited mixing policy and two batch distillation columns. Each flow is classified as a percentage of the total amount of every waste stream. Five classes are defined: ○ 0%, □ < 10%, ◘ 10-50%, ■ >50%, ● 100%. Streams S4 and S5 are not shown here because they are mainly sent either to distillation or incineration. The labels indicate the groups of solutions identified in Figure 8-11 (Pareto front groups are highlighted). The symbol x/z is used to denote that stream x is treated in the batch distillation column and stream z in the continuous distillation column.

Label	Streams to DIST	S1 to WWTP	S1 to WAO	S1 to INC	S2 to WWTP	S2 to WAO	S2 to INC	S3 to WWTP	S3 to WAO	S3 to INC
A	3/-	■	◘	◘	□	■	◘	□	◘	■
B	3/4	◘	■	□	□	◘	■	□	◘	■
C	3/5	◘	■	□	□	◘	■	□	◘	■
D	3/5	□	■	◘	□	■	◘	□	◘	■
E	3/5	◘	■	□	□	■	◘	□	◘	■
F*	3/5	□	■	◘	□	■	◘	□	□	■
G	4/5	■	◘	◘	□	■	◘	□	◘	■
H*	4/5	□	■	◘	□	■	◘	□	□	■
BC	4+5/-	●	○	○	○	●	○	○	○	●

Table 8-X : Optimization results for scenario 3 of CS1 (five waste streams S1-S5 [Table 4-I], two batch distillation columns, consideration of azeotropes). BC indicates the base case with limited mixing policy. Each flow is classified as a percentage of the total amount of every waste stream. Five classes are defined: ○ 0%, □ < 10%, ◘ 10-50%, ■ >50%, ● 100%. Streams S4 and S5 are not shown here because they are mainly sent either to distillation or incineration. The labels indicate the groups of solutions identified in Figure 8-12 (Pareto front groups are highlighted).

Label	Streams to DIST	S1 to WWTP	S1 to WAO	S1 to INC	S2 to WWTP	S2 to WAO	S2 to INC	S3 to WWTP	S3 to WAO	S3 to INC
A	4	■	□	□	□	◘	■	□	◘	■
B	5	■	□	□	□	◘	■	□	◘	■
C	3+4	◘	■	◘	□	■	◘	□	◘	■
D	3+5	□	■	◘	□	■	◘	□	□	■
E	4+5	■	◘	□	□	◘	■	□	◘	■
F*	4+5	□	■	◘	□	■	◘	□	◘	■
G*	4+5	□	◘	◘	□	■	◘	□	□	■
BC	4+5	●	○	○	○	●	○	○	○	●

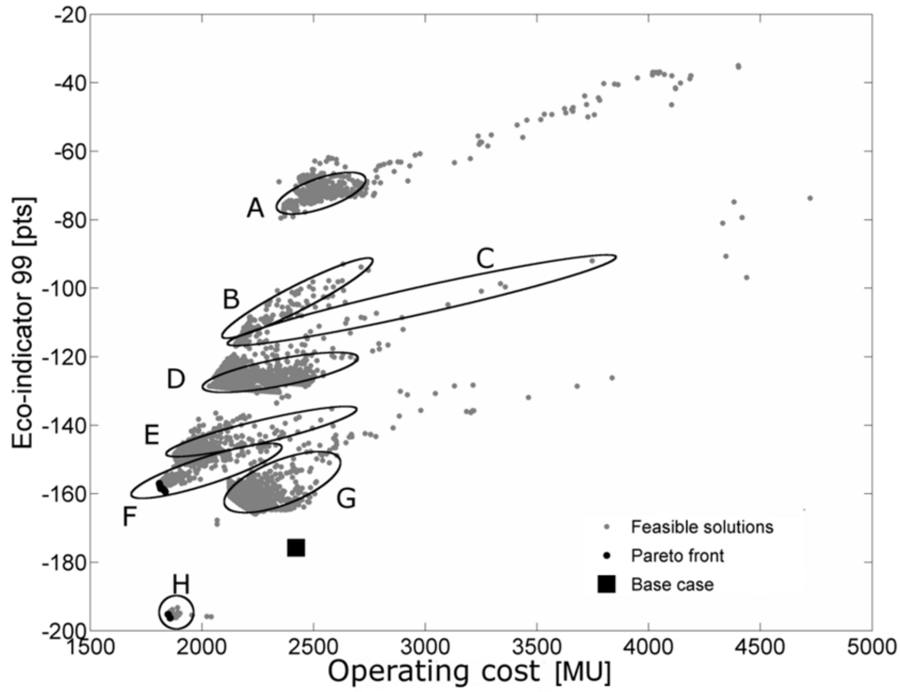

Figure 8-11 : Optimization results for scenario 2 of CS1 (five waste streams [Table 4-I], one batch and one continuous distillation column, no consideration of azeotropes). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points and the base case solution are highlighted. Groups of similar mixing solutions (A to H) are identified and their description is provided in Table 8-IX.

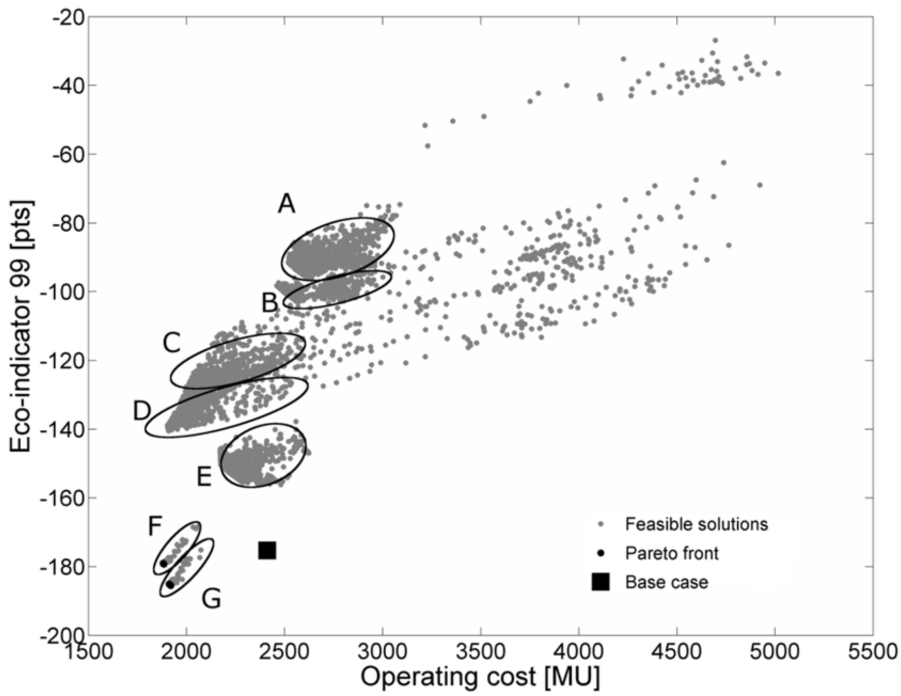

Figure 8-12 : Optimization results for scenario 3 of CS1 (five waste streams [Table 4-I], two batch distillation columns, including consideration of azeotropes). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points and the base case solution are highlighted. Groups of similar mixing solutions (A to G) are identified and their description is provided in Table 8-X.

J: Scenarios 2 and 3 of Case Study 2 (CS2)

Figure 8-13 and Figure 8-14 present the optimization results for the multi-period configurations of scenarios 2 and 3 in CS2 and Table 8-XI and Table 8-XII summarize the description of the groups of solutions. The distillation scenarios considered in the three multi-period configurations (see also Table 4-IV of the main text) are similar and, therefore, as described in the main text, it is the properly adjusted waste mixing that signifies the improvement in both objectives. Groups E and F, which are part of the Pareto front in both scenarios, differ only in the first period, with respect to the total waste loads to INC and WAO in scenario 2 and to all the treatment units in scenario 3. As a general trend, incineration is used in a large extent resulting in the most interesting solutions from the operating cost point of view, while shifting waste loads to WWTP and WAO allows the improvement of environmental impact, thus denoting a trade-off. However, it should also be noted that the amount and type of shifting the waste loads depends on the multi-period configuration that defines the availability of the waste streams.

Table 8-XI : Optimization results for scenario 2 of CS2 (five products P1–P5 in two production periods P1P3-P2P4P5, twelve waste streams [Table 4-II], two batch distillation columns, no azeotropes). BC indicates the base case with limited mixing policy. Each overall flow to a specific treatment unit for a given solution is classified as larger or smaller than the median of all solutions for this specific treatment unit (reported in the table). The labels indicate the groups of solutions identified in Figure 8-13 (Pareto front groups are highlighted).

Label	Streams to DIST	Flow to INC		Flow to WWTP		Flow to WAO	
		Period 1	Period 2	Period 1	Period 2	Period 1	Period 2
A	5,7,11	<25.6%	<21.7%	>9.3%	<17.6%	<5.9%	>3.7%
B	5,7,11	>25.6%	<21.7%	>9.3%	<17.6%	<5.9%	>3.7%
C	5,7,11	>25.6%	<21.7%	<9.3%	<17.6%	<5.9%	>3.7%
D	5,7,11	<25.6%	<21.7%	<9.3%	<17.6%	>5.9%	>3.7%
E*	5,7,11	>25.6%	>21.7%	>9.3%	>17.6%	<5.9%	<3.7%
F*	5,7,11	<25.6%	>21.7%	>9.3%	>17.6%	>5.9%	<3.7%
BC	5,7,11	18.4%	10.23%	22.0%	32.8%	0%	0%

Table 8-XII : Optimization results for scenario 3 of CS2 (five products P1–P5 in two production periods P2P3-P1P4P5, twelve waste streams [Table 4-II], two batch distillation columns, no azeotropes). BC indicates the base case with limited mixing policy. Each overall flow to a specific treatment unit for a given solution is classified as larger or smaller than the median of all solutions for this specific treatment unit (reported in the table). The labels indicate the groups of solutions identified in Figure 8-14 (Pareto front groups are highlighted).

Label	Streams to DIST	Flow to INC		Flow to WWTP		Flow to WAO	
		Period 1	Period 2	Period 1	Period 2	Period 1	Period 2
A	5,7	>30.2%	>8.5%	>0.7%	<31.9%	<11.9%	>0.2%
B	5,7,11	>30.2%	>8.5%	>0.7%	<31.9%	<11.9%	>0.2%
C	5,7,11	<30.2%	>8.5%	>0.7%	<31.9%	<11.9%	>0.2%
D	5,7,11	>30.2%	>8.5%	>0.7%	<31.9%	<11.9%	>0.2%
E*	5,7,11	>30.2%	>8.5%	>0.7%	>31.9%	<11.9%	<0.2%
F*	5,7,11	<30.2%	>8.5%	<0.7%	>31.9%	>11.9%	<0.2%
BC	5,7,11	21.3%	7.42%	21.6%	33.2%	0%	0%

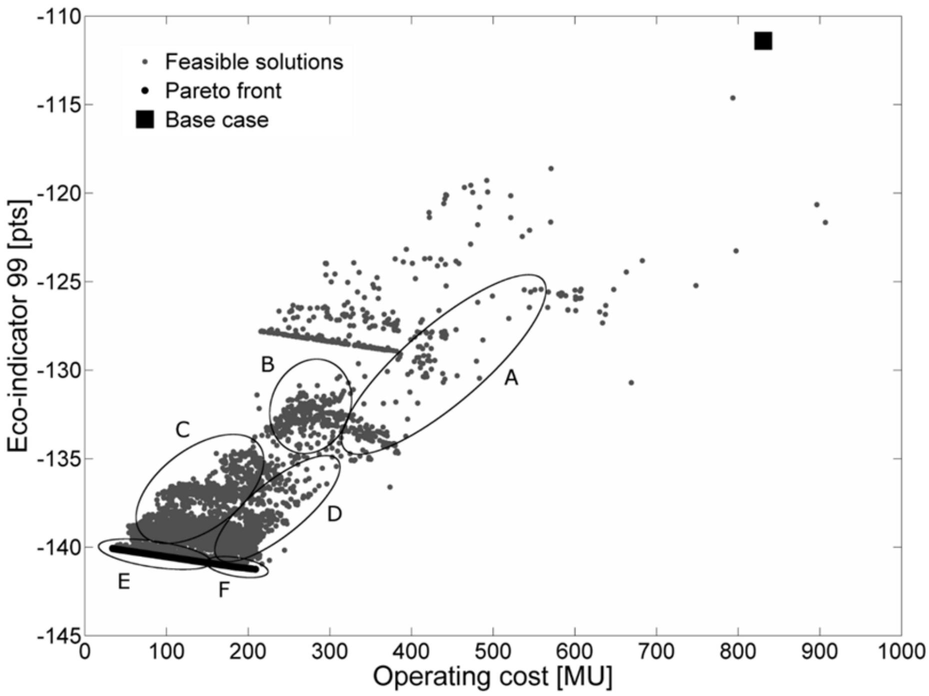

Figure 8-13 : Optimization results for scenario 2 of CS2 (five products P1–P5 in two production periods P1P3-P2P4P5, twelve waste streams [Table 4-II], two batch distillation columns, no azeotropes). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points and the base case solution are highlighted. Groups of similar mixing solutions (A to F) are identified and their description is provided in Table 8-XI.

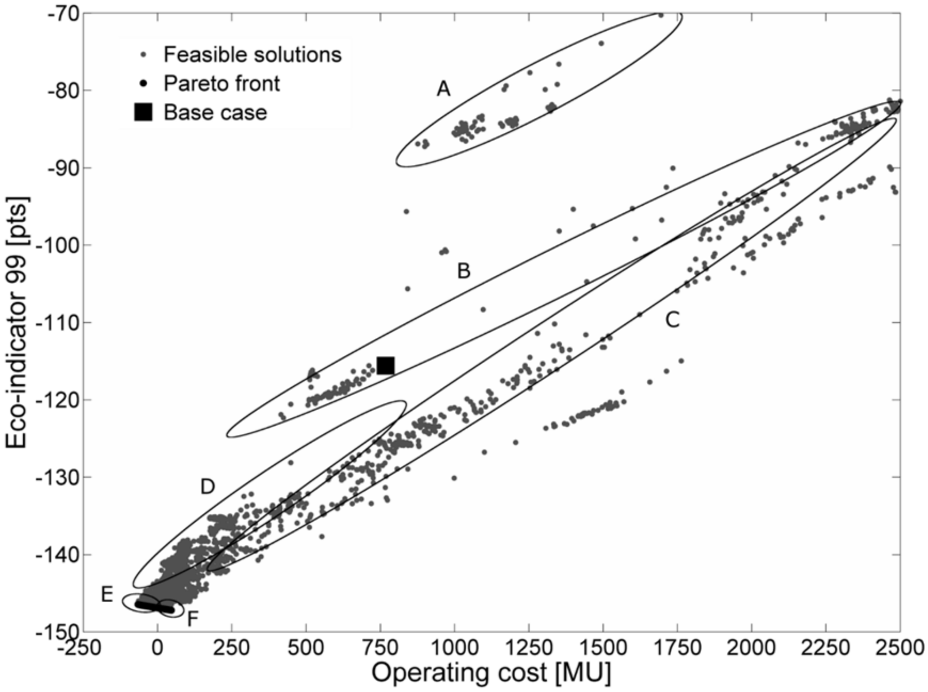

Figure 8-14 : Optimization results for scenario 3 of CS2 (five products P1–P5 in two production periods P2P3-P1P4P5, twelve waste streams [Table 4-II], two batch distillation columns, no azeotropes). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points and the base case solution are highlighted. Groups of similar mixing solutions (A to F) are identified and their description is provided in Table 8-XII.

K: Decomposition of auxiliary and energy related environmental impact and treatment unit cost for Case Study 1 (CS1)

A relative comparison of the auxiliary related environmental impact subcategories for scenarios 1 to 3 of CS1 with respect to the best cost and environmental solutions analyzed in Figure 4-5 and Figure 4-3 of the main text indicates the importance of the recovered solvents, followed by the sodium hydroxide used in WAO (Figure 8-15). The steam produced by incineration, and the natural gas consumption dominate the energy related environmental impact compared to the base case (Figure 8-16). The cost savings with respect to the treatment units are mainly due to the decrease in the use of WAO (Figure 8-17).

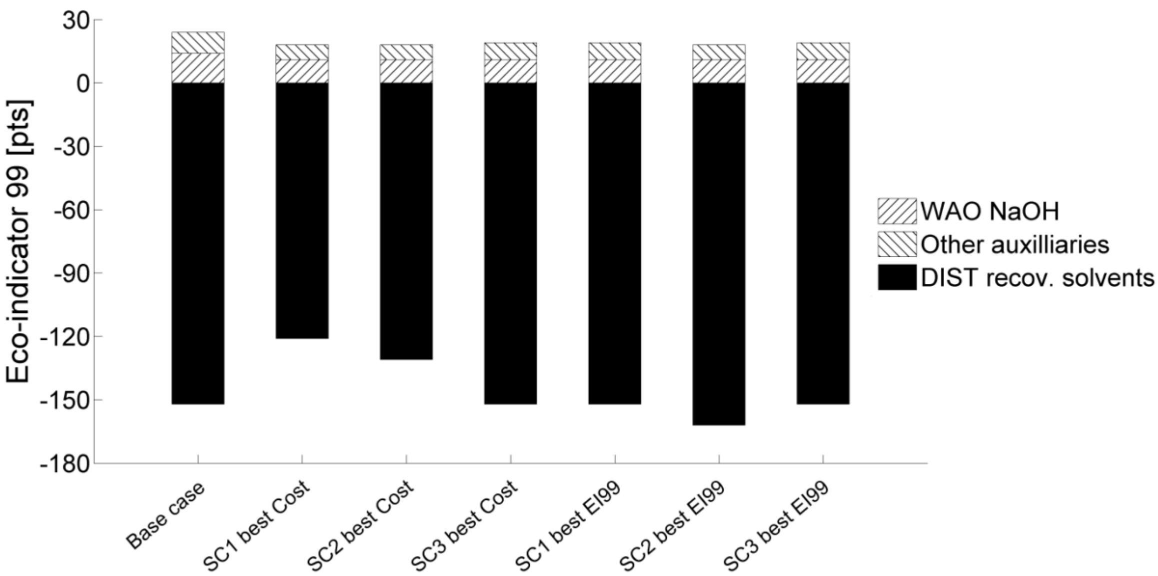

Figure 8-15 : Decomposition of the auxiliary related environmental impact for scenarios 1 to 3 of CS1 with respect to the best cost and environmental solutions analyzed in Figure 4-5 and Figure 4-3 of the main text.

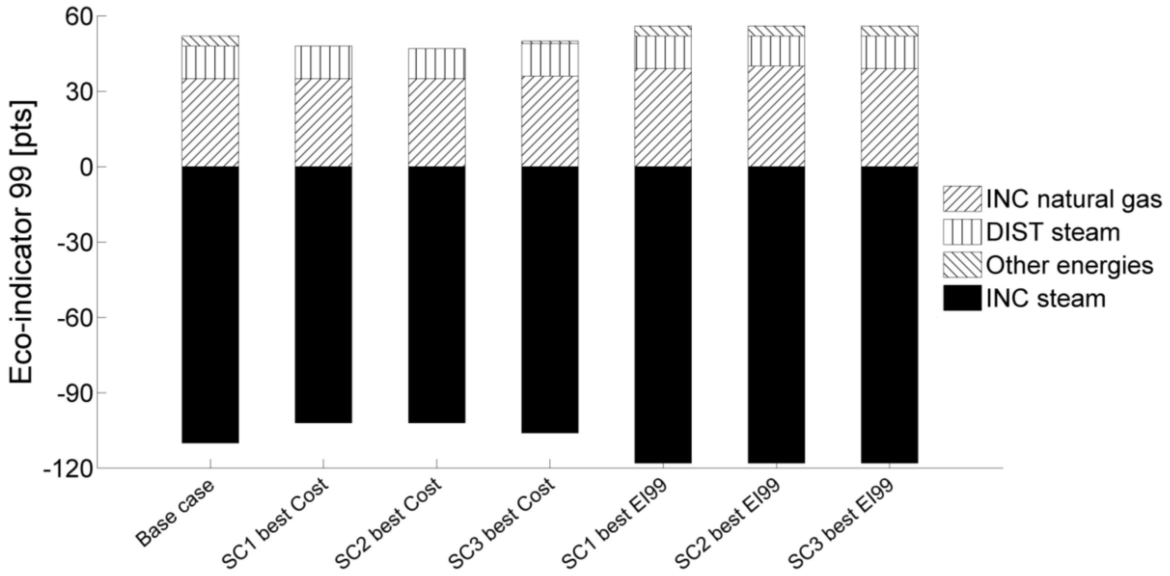

Figure 8-16 : Decomposition of the energy related environmental impact for scenarios 1 to 3 of CS1 with respect to the best cost and environmental solutions analyzed in Figure 4-5 and Figure 4-3 of the main text.

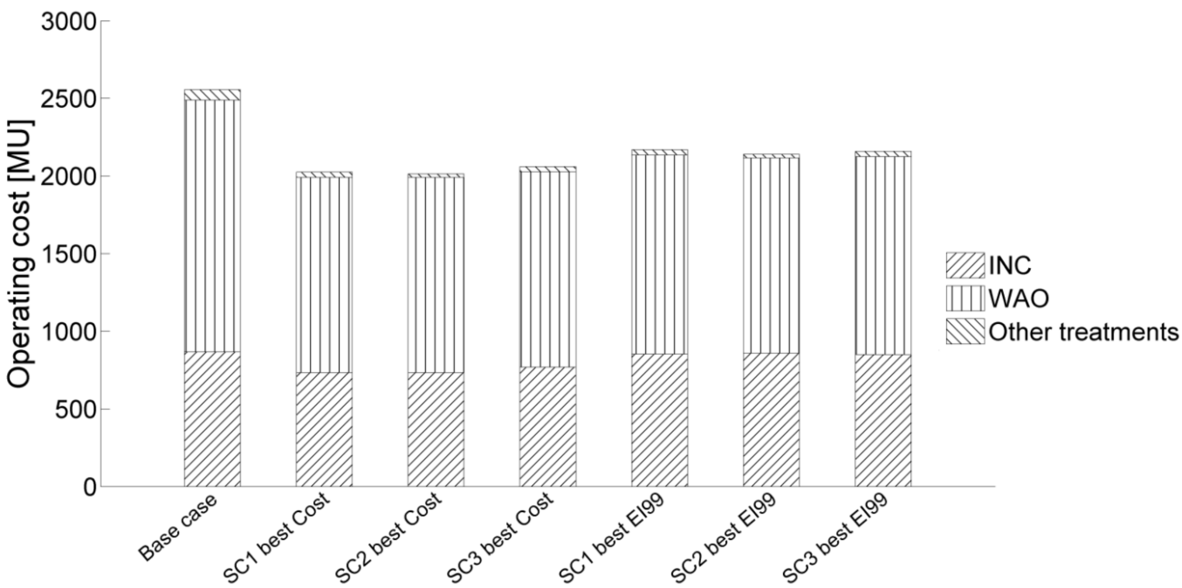

Figure 8-17 : Decomposition of the treatment unit related cost for scenarios 1 to 3 of CS1 with respect to the best cost and environmental solutions analyzed in Figure 4-5 and Figure 4-3 of the main text.

L: Remark on the LCIA models used for the INC sludge

For the disposal impact, an important factor is the sodium fate in the INC. The original model of INC (Seyler et al., 2005) does not include sodium in its fate description, and therefore in this work this is defined according to the Ecoinvent report for hazardous waste incineration (Doka, 2007). Sodium is mainly released as incineration residue (combustion lava) in solid form and then considered as part of the sludge from heavy metal precipitation. The amount of sludge is not defined from a mass balance but it is proportional to the mass of solid residue in order to take account of water content and co-precipitants. With the addition of wastewater streams with high content of sodium salts in the INC, which were originally defined to be sent to WWTP, the amount of incineration residue to dispose increases significantly, leading to higher disposal impact.

However, if no catalyst is present in the input stream of INC, no metal precipitation is needed. Without heavy metals, no solid residue or sludge has to be disposed, since, due to waste properties, combustion lava can be removed with washing water after neutralization. This reduces the impact for the residue disposal and saves auxiliaries used for precipitation. Therefore, when the waste management system does not accept heavy metal contaminated waste streams to be sent to INC, a correction factor (from 60 to 99% depending on the case) for the mass to be disposed has to be applied reducing the disposal impact in all scenarios and base cases. As the value for disposal impact is generally small, the overall results are not affected. Similarly, for the cost, this correction represents a reduction of 0.8–1.5 MU. No correction is needed for the impact or cost of auxiliaries, because their consumption is only determined by the mass of heavy metals.

M: Operating constraints and emissions for utility generation units

Table 8-XIII: Inventory of emissions, auxiliary and utility consumptions for the utility units base on ecoinvent database or on industrial sources ([a] amount of pollutant per MJ of burnt natural gas for steam production).

Unit	Auxiliary/utility/emission	Value	Unit	Source
Industrial water network	$FeCl_3$ 40%	20.00	mg/l	Industry
	Flocculant	4.00	ml/m^3	Industry
	NaOCl 15%	3.39	mg/l	Industry
	Electricity	4.29E-04	kWh/kg	ecoinvent
	Raw water	1.13	kg/kg	ecoinvent
Deionized water network	Industrial water	1.11	l/l	ecoinvent
	HCl 30%	2.40E-04	kg/kg	ecoinvent
	NaOH 50%	1.20E-04	kg/kg	ecoinvent
	Electricity	4.50E-04	kWh/kg	ecoinvent
	Anionic resin	8.23E-07	kg/kg	ecoinvent
	Cationic resin	1.84E-06	kg/kg	ecoinvent
	Na^+ to water	7.00E-05	kg/kg	ecoinvent
	Cl^- to water	2.30E-04	kg/kg	ecoinvent
	Waste heat	1.62E-03	MJ/kg	ecoinvent
Steam boiler	Deionized water	1.17	kg/kg	ecoinvent
	Natural gas	1.04	MJ/MJ	ecoinvent
	Electricity	8.00E-03	kWh/MJ	ecoinvent
	CO	1.04E-5	kg/MJ [a]	ecoinvent
	CO_2	5.60E-2	kg/MJ [a]	ecoinvent
	NOx	1.60E-6	kg/MJ [a]	ecoinvent
	PAH	1.00E-8	kg/MJ [a]	ecoinvent
	SO_2	5.50E-7	kg/MJ [a]	ecoinvent
	Particules	1.00E-7	kg/MJ [a]	ecoinvent
Compressed air network	Mineral oil	2.08E-08	kg/Nm^3	ecoinvent
	Mineral oil to waste	2.08E-08	kg/Nm^3	ecoinvent
	Electricity	1.49E-01	kWh/Nm^3	ecoinvent

Table 8-XIV: Maximal flow for the utility generation units.

Unit	Maximal flow	Unit
Industrial water network Cooling water network	1150	kg/s
Deionized water network	35	kg/s
Natural gas network (4.5 bar)	0.26	kg/s
Air network (7 bar)	35	kg/s
Electricity network	10	MW
Steam boiler	11	kg/s

N: Pareto fronts of Case 1

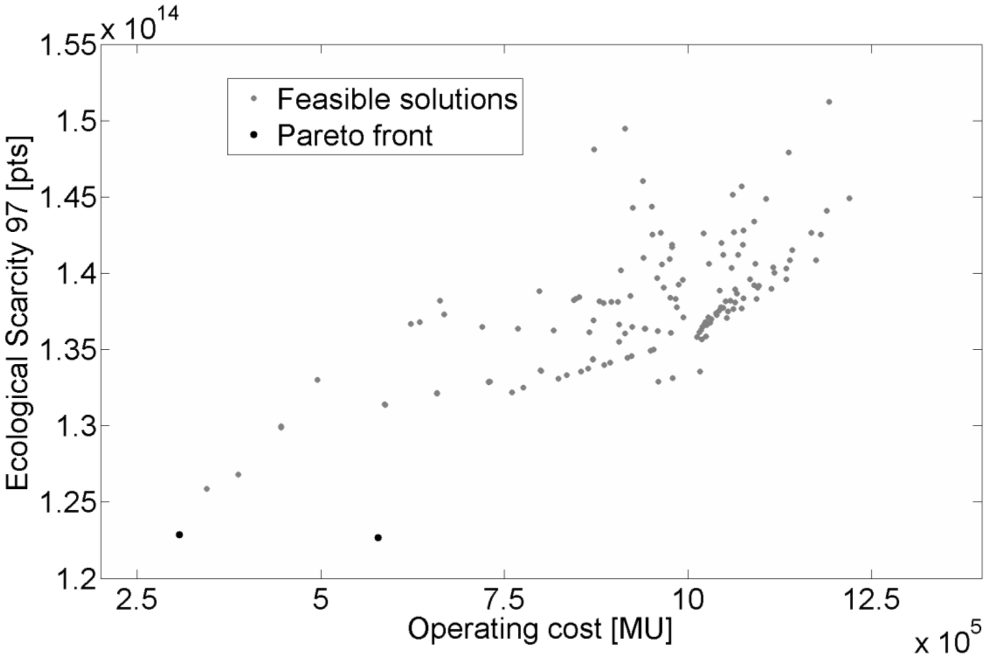

Figure 8-18 : Optimization results for scenario S4 (4 periods with UBP as environmental indicator). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points are highlighted.

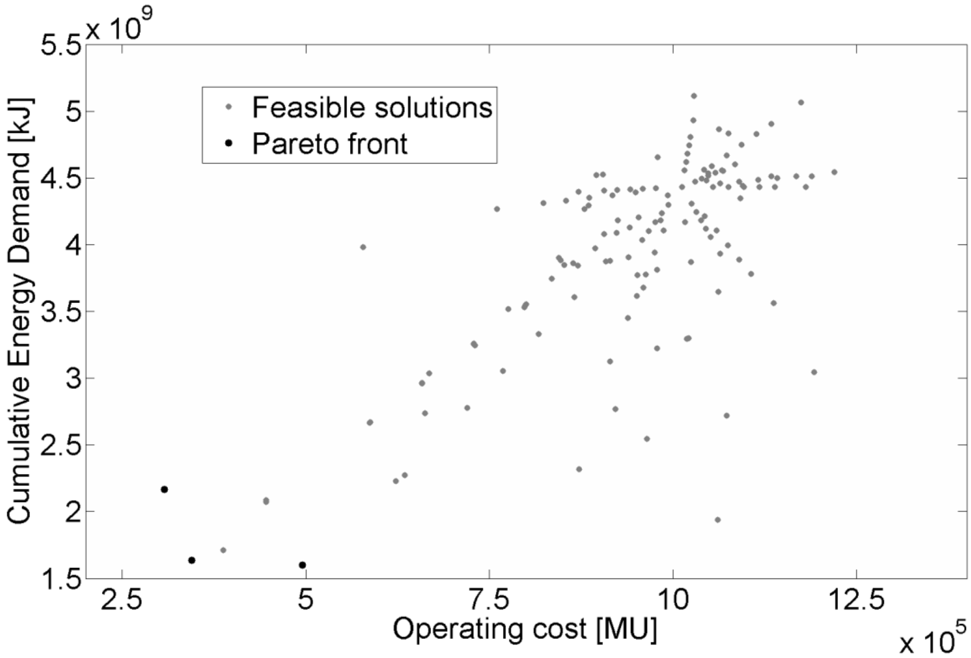

Figure 8-19 : Optimization results for scenario S5 (4 periods with CED as environmental indicator). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points are highlighted.

O: Pareto fronts of Case 2

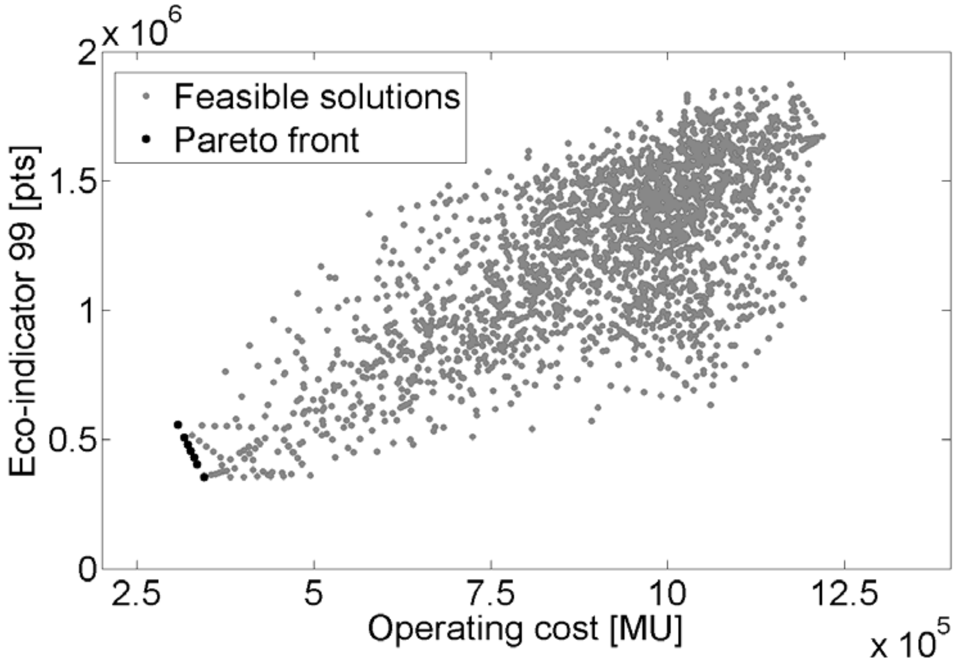

Figure 8-20 : Optimization results for scenario S2 (5 periods with ei99 as environmental indicator). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points are highlighted.

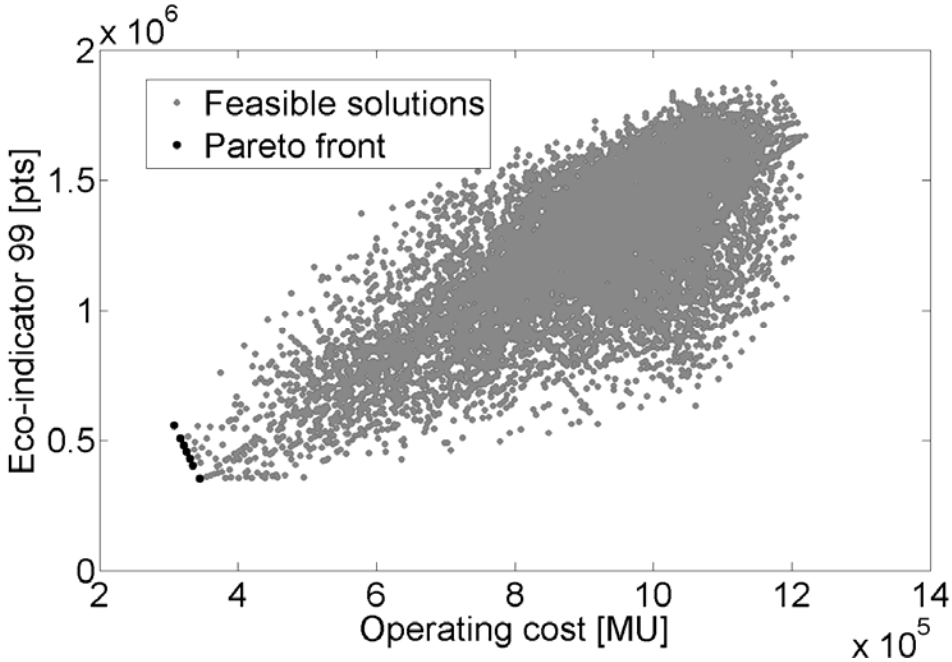

Figure 8-21 : Optimization results for scenario S3 (6 periods with ei99 as environmental indicator). Each point represents the multi-objective performance of a different mixing solution (the operating cost is given in arbitrary monetary units [MU]). Pareto optimal points are highlighted.

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1999-2001 1st Propedeutic of Diploma of chemist
University of Lausanne

1996-1999 Maturity (University entrance): science
Lycée cantonal de Porrentruy

Professional experience

2012- Production engineer
BASF, Monthey

2007-2012 Teaching assistant at ETHZ in process development and introduction in chemistry
ETHZ, Zurich

2006-2007 Calorimetric studies of microbiological reactions
Development of a biocalorimeter and study by calorimetry of the replication of phages.
Measure of the heat production (ITC) of bacteria assimilation by protists
UFZ, Leipzig (D)

2005-2006 Development of an e-learning course for students
Introduction of a new method for teaching thermal behaviour of reactors in collaboration with Wageningen University (e-learning course with interactive simulations)
EPFL, Lausanne/ Wageningen University, Wageningen (NL)

2004-2004 Semester project at LGCB
Encapsulation of oil and kinetic study of the degradation of the oil by enzyme
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Publications

- Rerat, C.;Papadokonstantakis, S.; Hungerbühler, K.; "Integrated waste management in batchchemical industry based on multi-objective optimization", Journal of the Air and Waste Management Association, **63**, 349–366
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