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Retrofit Design of Continuous Chemical Processes for the Improvement of Production Cost-Efficiency

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Le premier était de ne recevoir jamais aucune chose pour vraie que je ne la connusse évidemment être telle [...].

Le second, de diviser chacune des difficultés que j'examinerais en autant de parcelles qu'il se pourrait et qu'il serait requis pour les mieux résourdre.

Le troisième, de conduire par ordre mes pensées, en commençant par les objets les plus simples [...].

Et le dernier, de faire partout des dénombrements si entiers et des revues si générales, que je fusse assuré de ne rien omettre.

René Descartes, *Discours de la Méthode* (1637)

To my Parents
and Siss

PREFACE

Well now, how should I start? There is a seemingly uncountable number of people to whom I am very much indebted for help, advice, good food, and a lot of other things during my time as a graduate student. It seemed to me at the beginning that conducting a Ph.D.-thesis is a work of an individual – of course – now I know it is not so. In fact, quite the contrary... . I owe all of you very much.

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I am also very grateful to Jules Jeisy who not only initiated and provided me with a project partner within the Swiss chemical industry but also whom I like to think of as my industrial coach. This "down-to-earth" part of the thesis was decicive for finding an equilibrium between academia an industry.

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Finally and most importantly, I should say, I am grateful from the bottom of my heart to my parents and my sister Viviane for their never ending love and unwavering support in so many ways throughout all this time.

ABSTRACT

During the last decades chemical industry has had to face growing competition driven by rapid globalization, rising public concern for the environment, and increasing regulatory efforts of national governments concerning the environment, health, and safety. In response to these conditions and with regard to the capital intensive nature of chemical industry, constant optimization through redesign of existing production plants has emerged as a key strategy. This task is known as *retrofitting* and is especially carried out on continuous processes for the production of bulk products. According to a recent market survey 85% of all capital expenditures of the U.S.-chemical industry in plants and equipment are directed to retrofit projects while only 15% are invested into building new production plants. Despite the importance of retrofitting, only few methods address the systematic development of retrofit projects in view of *retrofit incentives* such as better production cost-efficiency, better environmental performance, or improved regulatory compliance of existing continuous production plants.

This thesis proposes a new systematic screening method for the design of *retrofit options* that aim at improving the production cost-efficiency of a continuous process and supports decision making when selecting the most profitable options. The screening method follows an evolutionary approach and combines process insights, process-specific knowledge, and general engineering practice with mathematical analysis. This is accomplished by introducing systematic procedures and evaluation tools in the three phases of the screening method: *analysis* of the existing process, *generation* of retrofit options, and detailed economic *evaluation* of these options for decision purposes.

In the *analysis* phase, a characteristic base case of the investigated process is defined and visualized using an appropriate graph representation. This representation allows the use of algorithms derived from graph theory in order to decompose the flow of components in the process flowsheet into open or cycle trajectories (paths) of single components. These component path flows are then assessed with an indicator framework that includes two indicators to

measure economic performance with regard to variable production costs and two more indicators to measure physico-chemical properties.

In the *generation* phase, the most important component path flows from an economic perspective are systematically investigated using a list of generic retrofit actions specifically formulated for improving the overall production cost-efficiency. The physico-chemical indicators are thereby used to pre-select generic retrofit actions from the complete list of actions. In conjunction with process-specific and engineering knowledge this procedure leads to promising *retrofit options*, i.e. by identification of important cost-sensitive operating parameters (optimization parameters) and by generation of structural modifications of the flowsheet topology (structural retrofit alternatives). The impact magnitude of each retrofit option on the variable process costs (total cost impact potential) is then roughly evaluated and can be used to limit the number of retrofit options for further investigation.

In the final *evaluation* phase, the selected operating parameters are studied in more detail by means of rigorous process flowsheet simulation and local sensitivity analysis before the variable process costs are minimized in a parameter optimization (optimized base case). Undesirable process constraints encountered during this procedure are then used to generate additional structural retrofit alternatives. Further on, attainable cost savings are calculated by sensitivity analysis for all structural retrofit alternatives relative to the optimized base case. The alternatives that incur the highest cost savings are selected and detailed plant modifications (technical implementation scenarios) formulated based on general engineering knowledge and experience. The variable process costs are then minimized for the best technical implementations scenarios by parameter optimization, the compliance with safety, health, and environmental criteria is assessed, and the profitability is calculated for each technical implementation scenario. Based on these results the decision maker can select the most profitable scenarios.

Two case studies, the hydro-dealkylation process for the manufacture of benzene (HDA case study) and an industrial process from the fine chemical industry (Fine Chemical case study) were used to demonstrate the capabilities of the proposed screening method. The application of the screening method to the HDA case study led to the identification of two optimization parameters and the generation of one structural retrofit alternative that exhibited far higher total cost impact potentials than any other retrofit option. These findings are in accordance with results from earlier studies in literature. In the case of the Fine Chemical process several retrofit options were generated that had been previously identified by the plant engineers. Especially two structural retrofit alternatives showed much higher attainable cost savings in the evaluation phase than expected.

ZUSAMMENFASSUNG

Während der letzten Jahrzehnte wurde die chemische Industrie mit wachsendem internationalen Wettbewerb (rasche Globalisierung der Märkte), zunehmendem Umweltbewusstsein der Öffentlichkeit und sich verschärfenden nationalen Verordnungen zu Umweltschutz, Gesundheit und Sicherheit konfrontiert. Als Reaktion auf die veränderten Rahmenbedingungen und unter Berücksichtigung der kapitalintensiven Struktur der chemischen Industrie wurde die Optimierung existierender Produktionsanlagen durch ständigen Umbau zu einer der wichtigsten Strategien. Diese Strategie, die im angelsächsischen Sprachgebrauch unter dem Namen *Retrofitting* bekannt ist, wird vor allem auf kontinuierliche Produktionsprozesse von Grossprodukten angewendet. Laut einer kürzlich erschienenen Marktanalyse werden 85% des Kapitalaufwands der chemischen Industrie in den USA in der Kategorie Anlagen & Apparate für Retrofit-Projekte ausgegeben und nur 15% zum Bau neuer Produktionsanlagen. Obwohl das Retrofitting kontinuierlicher Produktionsprozesse von grosser Bedeutung ist, gibt es dennoch nur wenige Methoden, die eine systematische Entwicklung von Retrofit-Projekten hinsichtlich Zielsetzungen wie niedrigere Produktionskosten, besserer Umweltschutz oder Erfüllung neuer Betriebsstandards unterstützt.

Diese wissenschaftliche Arbeit führt eine neue, systematische Screening-Methode zur Entwicklung von Retrofit-Optionen für kontinuierliche, chemische Prozesse im Hinblick auf Kosteneffizienzsteigerung ein und liefert Entscheidungshilfen zur Auswahl der wirtschaftlichsten Alternativen. Die Screening-Methode basiert auf einem evolutionären Lösungsansatz und verbindet dabei Prozessverständnis und Anlagenerfahrung mit mathematischer Analyse. Dies wird erreicht durch die Einführung einer systematischen Vorgehensweise und die Entwicklung von Hilfswerkzeugen in den drei Phasen der Screening-Methode: *Analyse* des bestehenden Prozesses, *Generierung* von *Retrofit-Optionen* und detaillierte wirtschaftliche *Bewertung* dieser Optionen zum Zweck der Entscheidungsfindung.

In der *Analysenphase* wird ein typischer Betriebszustand (Basisfall) des zu untersuchenden Prozesses festgelegt und durch eine geeignete Darstellung aus dem Bereich der Graphentheorie abgebildet. Diese Darstellung ermöglicht die Anwendung von Algorithmen der Graphentheorie zur Zerlegung des Prozess-Fliessbilds in offene oder geschlossene Ströme einzelner Komponenten. Diese Komponentenströme werden mit Hilfe eines Indikatorsystems bewertet, wobei zwei Indikatoren eine wirtschaftliche Bewertung in Bezug auf variable Produktionskosten und zwei weitere Indikatoren eine Bewertung physikalisch-chemischer Eigenschaften erlauben.

In der *Generierungsphase* werden die kostenintensivsten Komponentenströme mit einer Liste generischer Retrofit-Handlungsalternativen untersucht, die spezifisch auf die Verbesserung der Produktionskosteneffizienz abzielen. Die physikalisch-chemischen Indikatoren dienen hierbei zur Vorselektierung geeigneter Handlungsalternativen aus der Gesamtheit aller Alternativen. In Verbindung mit Prozessverständnis und Anlagenerfahrung führt diese Prozedur zu Retrofit-Optionen, einerseits durch Identifizierung der wichtigsten kostensensitiven Betriebsparameter (Optimierungsparameter) und andererseits zur Generierung von Prozessalternativen, die nur durch Anlagenumbau erreicht werden können (strukturelle Retrofit-Alternativen). Die Grössenordnung des Einflusses jeder Retrofit-Option auf die variablen Prozesskosten (Einflusspotentiale) wird dann grob evaluiert, damit die Anzahl an Retrofit-Optionen, die einer späteren, detaillierten Bewertung unterzogen werden, eingeschränkt werden können.

In der abschliessenden *Bewertungsphase* werden die selektierten Optimierungsparameter unter Anwendung rigoroser Prozesssimulation und lokaler Sensitivitätsanalyse untersucht, bevor die variablen Prozesskosten durch Parameteroptimierung anschliessend minimiert werden (optimierter Basisfall). Die im Laufe dieser Prozedur entdeckten Prozessrandbedingungen werden weiterhin verwendet, um zusätzliche strukturelle Retrofit-Alternativen zu generieren. Desweiteren werden die erzielbaren Kosteneinsparungen mittels Sensitivitätsanalyse für alle strukturellen Retrofit-Alternativen im Vergleich zum optimierten Basisfall berechnet. Die Alternativen mit den höchsten

Kosteneinsparungen werden ausgewählt und konkrete Umbaumassnahmen (Umbauszenarien) mit Hilfe allgemeiner ingenieurtechnischer Kenntnisse und Erfahrung vorgeschlagen. Die variablen Prozesskosten werden im folgenden für die besten Umbauszenarien durch Parameteroptimierung minimiert, die Übereinstimmung mit Sicherheits-, Gesundheits- und Umweltschutzanforderungen überprüft und die Profitabilität der einzelnen Umbauszenarien berechnet. Der Entscheidungsverantwortliche ist damit in der Lage, die profitabelsten Umbauszenarien aufgrund dieser Ergebnisse auszuwählen.

Zwei Fallbeispiele, der Prozess zur Herstellung von Benzol durch Hydrodealkylierung von Toluol (HDA-Fallbeispiel) und ein industrieller Prozess der Feinchemikalien-Industrie (Feinchemie Fallbeispiel), wurden eingesetzt, um die Vorteile der vorgestellten Screening-Methode zu demonstrieren. Die Anwendung der Screening-Methode auf das HDA-Fallbeispiel führte zur Identifikation von zwei Optimierungsparametern und zur Generierung einer strukturellen Retrofit-Alternative, die wesentlich höhere Einflusspotentiale offenbarten als alle anderen Retrofit-Optionen. Diese Ergebnisse stehen in Einklang mit Resultaten früherer Studien in der Literatur. Im Falle des Feinchemikalien-Prozesses wurden mehrere Retrofit-Optionen generiert, die zuvor von Betriebsingenieuren identifiziert wurden. Besonders zwei strukturelle Retrofit-Alternativen wiesen wesentlich höhere erzielbare Kosteneinsparungen in der Bewertungsphase auf als erwartet.

RÉSUMÉ

Au cours des dernières décennies, l'industrie chimique s'est vue confrontée à une concurrence en progression constante dûe à une globalisation rapide, mais également à de nouvelles problématiques vu le souci croissant du public pour l'environnement et le développement des lois nationales concernant l'environnement, la santé et la sécurité. En réponse à ces conditions et en considération des coûts élevés encourrus dans l'industrie chimique, l'optimisation permanente des procédés de fabrication s'est avérée constituer une stratégie cruciale. Cette méthode, connue sous le nom de *retrofitting* en anglais, s'applique en particulier aux procédés continus (donc aux produits de masse). D'après une étude de marché récente, près de 85% de toutes les dépenses de l'industrie chimique des USA dans la catégorie installations et équipements sont consacrées à des projets de retrofitting, alors que 15% seulement sont dévolues à la construction de nouvelles chaînes de production. En dépit de l'importance du retrofitting il n'existe que peu de méthodes consacrées au développement systématique de tels projets visant des objectifs tels qu'une meilleure efficience économique de la production, qu'une meilleure performance environnementale ou qu'une conformation aux réglementations pour la santé et la sécurite.

Ce travail de recherche propose une nouvelle méthode systématique de *screening* pour l'identification d'options de retrofit dont le but est d'améliorer l'efficience économique de la production d'un procédé en continu et qui offre également une aide à la prise de décision lors de la sélection des options les plus profitables. Cette méthode de screening suit une approche hiérarchique et combine les résultats d'une analyse mathématique d'un procédé, les connaissances spécifiques tirées de l'expérience des ingénieurs de production et des connaissances générales en ingénierie. Ceci est accompli en introduisant une procédure systématique et des outils d'évaluation dans les trois phases de la méthode de screening: *analyse* du procédé en opération (cas de base), *création* d'options de retrofit et *évaluation* économique détaillée de ces options en vue de la prise de décision.

Dans la phase d'*analyse*, un cas de base caractéristique est d'abord défini et visualisé en utilisant une représentation tirée de la théorie des graphes. Cette représentation permet l'utilisation d'algorithmes dans le but de décomposer les flux de chaque composant en trajectoires ouvertes ou cycliques (boucles de recyclages). Ces trajectoires sont alors évaluées à l'aide d'une série d'indicateurs qui en comprend deux pour mesurer la performance économique par rapport aux coûts de production variables et deux pour en mesurer les propiétés physiques et chimiques.

Dans la phase de *création* d'options de retrofit, les trajectoires des composants les plus importants du point de vue économique sont examinées de façon systématique selon une liste d'actions génériques de retrofitting qui ont été spécifiquement élaborées pour améliorer l'efficience économique de la production. Les indicateurs physiques et chimiques y sont utilisés pour effectuer une pré-sélection des actions génériques parmi la liste complète des actions possibles. Cette procédure, qui a l'avantage de combiner des connaissances spécifiques du procédé à une expertise générale en ingénierie, aboutit à l'identification des paramètres operatifs qui ont une influence importante sur les coûts (paramètres d'optimisation) et à la génération de modifications structurelles de la topologie du procédé (alternatives structurelles de retrofitting). La répercussion de ces deux types d'actions de retrofitting sur les coûts variables du procédé peut alors être évaluée approximativement (impact total sur les coûts) et peut être utilisée afin de limiter, si nécessaire, le champ de décision aux options les plus prometteuses.

Dans la phase finale d'*évaluation*, les paramètres opératifs sélectionnés sont étudiés en plus grand détail au moyen d'une simulation de procédé rigoureuse et d'une analyse de sensibilité locale puis les coûts variables du procédé sont minimisées par une optimisation des paramètres (cas de base optimisé). Les contraintes indésirables rencontrées au cours de cette procédure sont alors utilisées pour générer de nouvelles alternatives structurelles de retrofitting. Ensuite, le calcul des économies de coûts réalisables est effectué par analyse de sensibilité pour toutes les alternatives structurelles de retrofit se rapportant au cas de base optimisé. Les alternatives qui offrent les meilleures possibilités de

limitation des coûts sont sélectionnées et les modifications détaillées de l'installation de production (scénarios de mise en œuvre technique) sont formulées par rapport à des connaissances générales ainsi qu'à l'expérience en matière d'ingénierie. Les coûts variables du procédé sont ensuite minimisés pour les meilleurs scénarios en utilisant les paramètres d'optimisation, la conformité aux critères de sécurité, de santé et d'environnement est evalué pour chaque scénario de mise en œuvre technique. En se basant sur ces résultats le décideur peut sélectionner les scénarios les plus profitables.

Deux études de cas, le procédé d' hydro-déalkylisation pour la fabrication de benzène (procédé HDA) ainsi qu'un procédé industriel de chimie fine, ont été utilitsés pour démontrer les capabilitées de la méthode de screening proposée. L'application de la méthode de screening au procédé HDA conduissait à l'identification de deux paramètres operatifs et à la création d'une alternative structurelle de retrofit qui montrait des impacts total sur les coûts plus haut que chaque autre option de retrofit. Ces découvertes correspondent aux résultats d'études précedentes dans la litérature. Dans cas du procédé de chimie fine plusieures options de retrofit ont été crées qui ont été identifiées précédemment par les ingénieurs de production. En particulier deux alternatives structurelles de retrofit démontraient des économies de coûts réalisables plus hautes que prévues.

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1 INTRODUCTION

1.1 Current challenges and trends in chemical industry

Chemical industry as one of the most capital intensive industries comprises a number of distinctive business sectors such as petrochemicals and basic products (commodities), polymers, speciality products, biotech products, pharmaceuticals, and more according to various classification criteria. Three of the major characteristics of these sectors consist in production quantities, cost structures, and profit margins. Petrochemicals as well as commodities and pharmaceuticals represent extremes with regard to these characteristics. While petrochemicals and basic products can be considered as bulk products manufactured in mass quantities with only little profit margins, pharmaceuticals are produced in small quantities but generate considerable profits. Currently, chemical industry is facing a number of important challenges affecting the aforementioned business sectors in different ways. Although the scope of this work is concerned with the continuous manufacture of bulk products in dedicated plants, some of the following statements are applicable to chemical industry in general.

1.1.1 Competition and globalisation

Many chemical plants for the production of bulk products were built in the past when profit margins could be kept large and thus were not typically designed to be most cost-efficient from a production cost perspective (Grossmann et al. (1987)[24]). Competition at that time rested on feedstock availability, cost structures, strategic site location and market access. Nowadays, an easier movement of capital, information technology, new production technologies, new markets, and different cost structures around the world (e.g. labour and raw material costs) are the driving forces of rapid internationalisation in chemical industry. On the one hand, globalization allows chemical industry to take advantage of larger markets and optimize its resources within a larger space of opportunities. On the other hand, globalization poses enormous competitive pressure on companies. Existing production facilities are increasingly subject to internal (inside a company) and external (between competing companies) benchmarking with respect to their production costs on a global scale. Moreover, the global interdependencies in chemical industry have made companies more vulnerable to global economic fluctuations. This ongoing development has greatly increased the need to redesign, modernize and continuously improve the cost efficiency and capacity of existing production facilities and has tremendously raised the standards in the design of new processes.

1.1.2 Environmental concerns

Increasing public awareness and coordinated efforts of local communities, regulatory agencies, and non-governmental agencies (NGOs) have exerted considerable influence on chemical industry to preserve the environment. As a response, chemical industry has changed its understanding of process design and operations. This includes strict measures to reduce emissions by waste treatment, remediation of environmental damages resulting from past production practices, banning of hazardous products, new internal waste-management guidelines, and information policies, among others. In addition, chemical industry constantly undertakes efforts to increase their resource efficiency from a raw material and energy point of view. The latter development is not only adopted to reduce the inherent ecological impact in process operations but also to reduce production costs and make production processes more profitable (Weizsäcker et al. (1996)**[65]**).

1.1.3 Regulations

National governmental regulations impact the business performance of chemical companies on different levels. Governments act on monetary and fiscal policies as well as on more specific policies with respect to e.g. environment and process safety. These regulations and policies are increasingly established in conformity with international agreements such as trade and integration treaties (e.g. World Trade Organization, European Union) and internationally accepted standardization procedures (ISO 9000 quality standards and ISO 14000 environmental management standards). Especially regulations on environmental protection and process safety have considerable impact on production costs in chemical industry. Therefore, companies seek to reduce this regulatory impact on their businesses by either complying with the regulators' objectives or even by undertaking pro-active measures to anticipate future objectives. A good example for the latter is the "Responsible Care"-initiative that is now adopted by numerous internationally operating chemical companies (Shanley et al. (1997)[58]).

1.2 Integrated process development, process life-cycle, and retrofitting

Process development is defined as the procedure that starts at the decision to produce a given chemical product and ends in the start-up of a fully operational plant for its production. Hungerbühler et al. (1999)[33] emphasize that in view of increasing competition, globalization, environmental concerns and regulations, multiple objectives have to be equally considered during *integrated* process development: economic as well as ecological efficiency (eco-efficiency), inherent safety, and social acceptance. According to Heinzle and Hungerbühler (1997)[31] process development generally follows a succession of different phases from the initial product idea to the operational plant: chemical research, process design, plant design, and startup (see Figure 1-1). In the chemical research phase, technically feasible synthesis routes for the desired product are investigated and important physico-chemical data on substances and reactions determined. In the process design phase a large number of process alternatives is formulated, evaluated, and the best alternatives selected (Hoffmann (2001)[32]). The plant design phase is then concerned with generating detailed mass and energy balances for the selected alternatives, identifying the best process alternative, designing process equipment, identifying the optimal process operating parameters, and finalizing the layout of the plant. In the last phase the chemical plant is built, started up and operated. Common

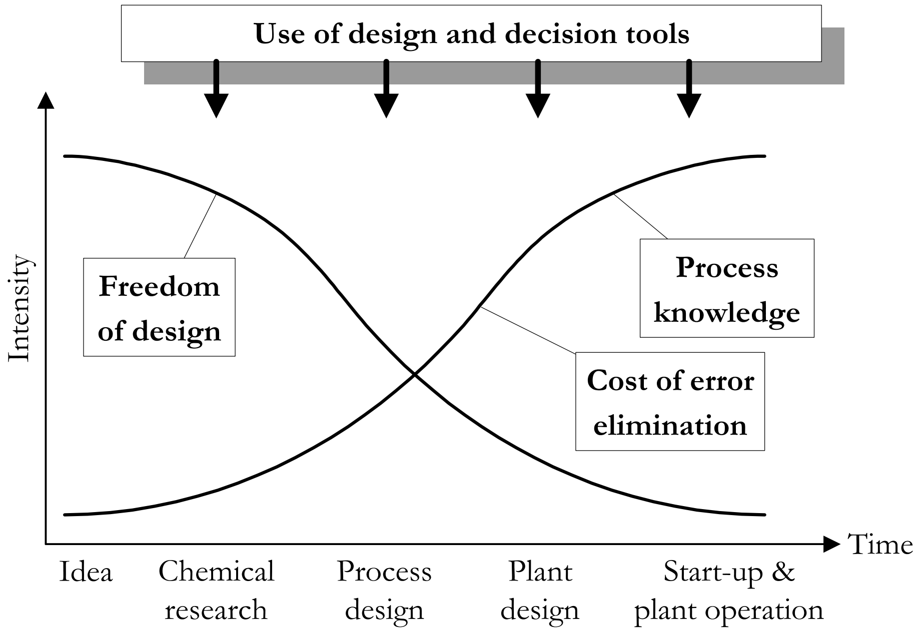


Figure 1-1: Degrees of freedom, depth of knowledge and cost of error elimination in process design (adapted from Heinzle and Hungerbühler (1997)[31])

characteristics of process development in early stages consist in having little process knowledge available when the most important decisions have to be taken. As process development proceeds (see Figure 1-1), degrees of freedom steadily decrease, while process knowledge is constantly gathered and the costs to eliminate errors made in earlier stages rapidly increases. For all phases of process development an abundant number of design and decision methods have been presented in literature to support the *decision-maker* (i.e. process engineer in charge of process development).

After entering the operational phase, particularly continuous processes with high production capacities are usally operated over long periods of time in order to make the often large capital investments profitable. Therefore, at some time in the process life-cycle new external and internal conditions, resulting from the constant challenges chemical industry is facing, necessarily take effect. In order to maintain a competitive position under these changing conditions, chemical process plants need to be adapted constantly. Typical examples of external and internal conditions and the *incentives* they imply include:

- Availability of more cost-efficient technologies on the market => *improvement of the cost-efficiency associated with production*
- Increase of product market demand => *capacity expansion of existing plants*
- New governmental regulations concerning the environment => *reduction of emissions*
- Reduced profit margins due to competition => *reduction of the variable costs of production*
- Increasing energy prices => *reduction of the energy costs of production*
- Improvement of operational practice => *modernization of equipment*
- Discovery of problematic safety issues => *implementation of new safety measures*
- Deterioration of plant equipment => *replacement of worn-out equipment*

This redesign task is known as *retrofitting* and includes a combination of the following types of modifications in order of increasing costs (Fisher et al. (1987)**[18]**):

a) **The operating conditions of the plant are altered:** No process equipment changes are needed and thus almost no investment costs are associated with this type of modification.

b) **The piping which connects an equipment is altered:** The equipment might be used for a new purpose. Repiping generally involves low investment costs.

c) **The flowsheet topology is unchanged but equipment is refitted:** Some equipment can be altered without having to replace it altogether. An example is the refitting of a distillation column with new column internals. This type of modifications can incur moderate investment costs.

d) **New equipment is added and old equipment decommissioned:** This type of modification can change the process flowsheet topology at usually considerable investment expenses.

The changes introduced differ in complexity and cost, yet are seldom associated with the major capital expenditures in building a new process plant.

Depending on which external or internal conditions arise, different *retrofit incentives* are developed in response by the process engineers in charge of a process plant. Figure 1-2 depicts a selection of retrofit incentives typically encountered in chemical industry. Often, multiple incentives are envisioned at the same time (e.g. raising the production capacity of the process and increasing its cost efficiency with regard to labour, capital, energy and raw material costs).

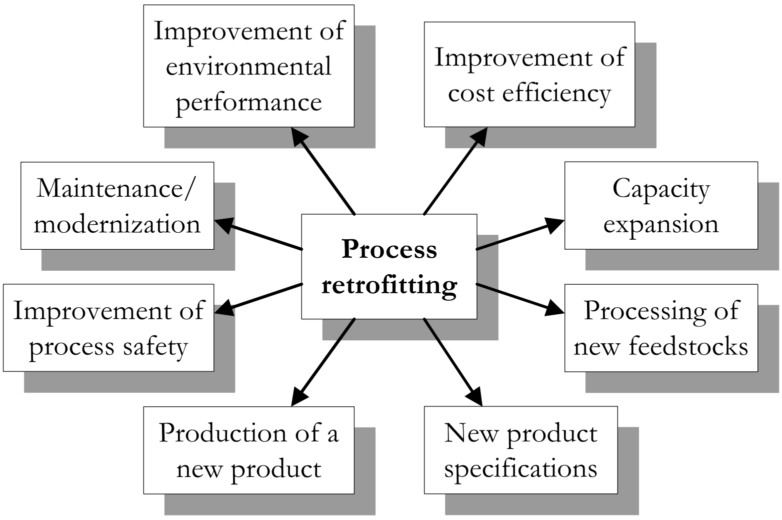


Figure 1-2: Selection of typical retrofit incentives for chemical processes

The development of a solution for a *retrofit problem*, from the incentive definition to the detailed plans for the necessary plant modifications, is very similar to the development of a new process. It also undergoes several steps as highlighted in Figure 1-3: definition of retrofit incentive, process retrofit design, plant redesign, and final implementation. As stated before, the decision-maker defines a retrofit incentive resulting from the currently experienced external and internal circumstances. In the *retrofit design* phase, the process then needs to be analyzed from the incentive's perspective, explicit *process retrofit alternatives* need to be generated, evaluated, and the best one(s) selected. This procedure is analogous to the process design phase during the development of new processes (often referred to as *grassroot design* or *greenfield design* in order to differentiate between the two types of design – see also Figure 1-1). Plant redesign further consists in setting up the final plans for modifying the existing process plant. Finally, in the implementation phase these modifications are introduced to the plant either while the plant is operating, during a routine plant shutdown for maintenance purposes, or even during a non-routine plant shutdown if unavoidable.

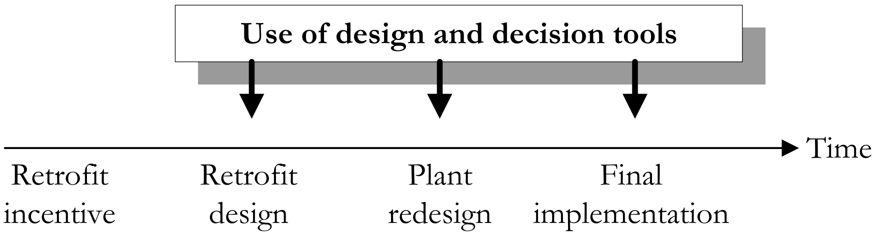


Figure 1-3: Development of a technical solution for a retrofit problem

During the mid 80's, Grossmann et al. (1987)**[24]** estimated that 70-80% of all process design projects were dealing with the retrofitting of existing production plants. Considering the importance of retrofitting, the existing literature on this specific subject is still sparsely represented today. Only few systematic design and decision methods are available to the decision-maker that tackle the complex task at the heart of a retrofit problem: *retrofit design*. The importance of retrofitting and the lack of systematic retrofit design methods are the motivations for this research work.

1.3 Challenges in retrofit design

Retrofit design is a complex task for several reasons. The following aspects are concerned with the basis of the retrofit problem, i.e. detailed knowledge and data about the process plant itself:

- **Process complexity:** Generally, continuous processes include a large number of process operating parameters associated with the plant equipment (e.g. temperatures, pressures, flow-rates). Although cause-effect relationships (interdependencies) between process operating parameters (e.g. reactor temperature) and dependent operating parameters (e.g. the conversion of the desired reaction depends on that temperature) are usually known by the process engineers operating the plant, often little systematic and quantified knowledge on cause-effect relationships (especially trade-offs such as energy vs. raw material costs) is available.

- **Process data:** Amazingly, in most continuous process plants data is only partially available on stream compositions, flow-rates, and operating conditions. Often, data on undesirable side-products is altogether missing or sparsely available. Further, the data is always subject to uncertainty since continuous processes never operate in a steady-state for various reasons: e.g. fluctuation of product demand, different raw material qualities, reaction of process control system to external disturbances.
- **Complex infrastructure:** Continuous process plants very often operate in a network of interdependent process plants. This adds even more complexity to the investigated process as feeds from other process plants can vary considerably or even stop if an external plant is shut down. Accordingly, data mining needs to be more extensive because ultimately multiple characteristic operating states of the plant might have to be considered.

In addition to these issues, retrofit design is subject to a number of inherent difficulties specifically due to the nature of retrofit problems:

- **Evaluation of a large number of process retrofit alternatives:** As in grassroot design, in principle an exhaustive number of process alternatives would have to be evaluated if all combinatorial arrangements of the four different types of modifications in retrofitting (repiping, modification of existing equipment, replacement of existing equipment, and addition of new equipment – see Section 1.2) were to be considered. However, a very high percentage of these alternatives will prove to be unsuitable after thorough evaluation.

- **Evaluation of the operability of equipment under new operating conditions:** Since when solving retrofit problems the decision-maker typically seeks to determine the least cost incurring process retrofit alternatives, the operability of existing equipment under new operating conditions needs to be evaluated. This task has to be performed in parallel to the evaluation of the large number of process retrofit alternatives and therefore adds considerable complexity to the overall retrofit design problem.
- **Few degrees of freedom in retrofit design:** As shown in Figure 1-1 the costs of error elimination in process design increases while the degrees of freedom in process design decrease. The same principle can be extended to retrofit problems. Once a plant is operating there are few degrees of freedom left to change plant operations without creating considerable costs.
- **Process retrofit alternatives have to comply with important criteria:** Any solution to a retrofit problem has to comply with criteria such as operability, safety and controllability. The operability of a given solution to the retrofit problem needs to be guaranteed with regard to e.g. low maintenance requirements and reliability. A solution also needs to comply with safety standards and thus should already be inherently safe without the need for expensive safety measures. Finally, the solution should not lead to problems in process control as this can have consequences on process safety, product quality specifications, and production capacity among others.

All of the aforementioned issues demonstrate the complexity associated with retrofit design. These complexities give rise to a number of important questions. The research work in this thesis is intended to provide answers to the following questions:

- *How can the time-consuming evaluation process of an exhaustive number of process retrofit alternatives be reduced?*
- *How can the chances of finding an optimal solution to a given retrofit problem be increased?*
- *How should a new retrofit design method be structured in order to encompass the different retrofit incentives and their combinations in a systematic manner (see Figure 1-2)?*
- *How can the heuristic knowledge gathered during the operating phase of the process be systematically incorporated into the solution of the retrofit problem?*
- *How should the new retrofit method be organized so that links and synergies with other process design methods (for grassroot and retrofit design) can be obtained?*

1.4 Thesis statement

The first hypothesis of this work is that promising process alternatives for a retrofit problem can be *directly* found by systematically *screening* the process with regard to an adequate performance measure for a given retrofit incentive or a combination of retrofit incentives. The results of such a screening should highlight retrofit alternatives for which improvement potentials exists. Only these then need to be tackled in search of promising solutions for the specific retrofit problem.

The second hypothesis is that a complex retrofit problem can be decomposed into a number of simpler sub-problems. The decomposition into sub-problems should help to understand interdependencies and trade-offs in the investigated process. Moreover, the analysis of these sub-problems should also support the decision-maker in generating promising retrofit alternatives combined with process-specific knowledge, general engineering knowledge, and best available practice. It is believed that a combination of both hypotheses can systematically guide the decision-maker through the retrofit problem as well as support the decision-maker in generating promising process retrofit alternatives.

The main objective pursued in this thesis targets the development of a systematic and transparent retrofit design method that specifically addresses retrofit problems, simultaneously identifies important operating parameters (for plant optimization without investments) and generates structural retrofit alternatives (includes discrete changes in the flowsheet topology), makes use of the aforementioned hypotheses, and tries to find answers to the questions formulated in the previous section. This new retrofit design method is later referred to as *screening method*.

1.5 Contributions to research

The thesis offers a number of contributions in the field of retrofit design in conjuction with the hypotheses and the thesis objective mentioned in the previous section:

- A screening method that has evolutionary characteristics is introduced for retrofit design of continuously operating processes. It systematically analyzes processes for improvement potentials, evaluates these by a modular indicator framework, and – combined with specific process knowledge as well as general engineering knowledge – supports the decision-maker in generating promising process retrofit alternatives. The core of the analysis procedure consists in shifting from a unit-operation-centered perspective to a perspective of the flow trajectory of individual components through the process. In this thesis an example of a typical retrofit incentive, i.e. the improvement of the production cost efficiency of a process, is selected.

- Sensitivity analysis and parameter optimization are introduced in the screening method as tools to evaluate the generated process retrofit alternatives in more detail and to support the decision-maker in selecting the alternatives with the highest chances of success.

- The screening method introduced above is applied to two different industrial case studies and promising process retrofit alternatives are generated. A profitability calculation for the implementation of two examplary process retrofit alternatives is performed.

1.6 Thesis outline

The thesis is structured in three main parts as shown in Figure 1-4. The first part which comprises Chapters 1 to 3 describes the research scope, the main thesis objectives, the contributions to research, the characteristics of grassroot and retrofit design methods, the position of the new retrofit design method among other process design methods, a summary of the structure of the new retrofit design method, and introduces two industrial case studies for later application.

The second part comprises Chapters 4 to 8 in which the new retrofit design method is introduced step by step. Each chapter contains an introductory part of basic knowledge required in the comprehension of the chapter, a theoretical part in which the central concepts are laid out, and a practical part in which the concepts are applied to the two case studies. Conclusions are also drawn in each chapter concerning the overall thesis objectives. Chapter 4 explains how a process is screened for improvement potentials with regard to a specific retrofit incentive (production cost efficiency). Chapter 5 describes the identification of important operating parameters and the generation of process retrofit alternatives (later referred to as *retrofit options*) from the findings of Chapter 4. In Chapters 7 and 8, these retrofit options are then evaluated in detail with mathematical tools.

In the final section, Chapter 9, the new retrofit design method is revisited and the results of the case studies summarized. Overall conclusions are then drawn and suggestions for future research are made.

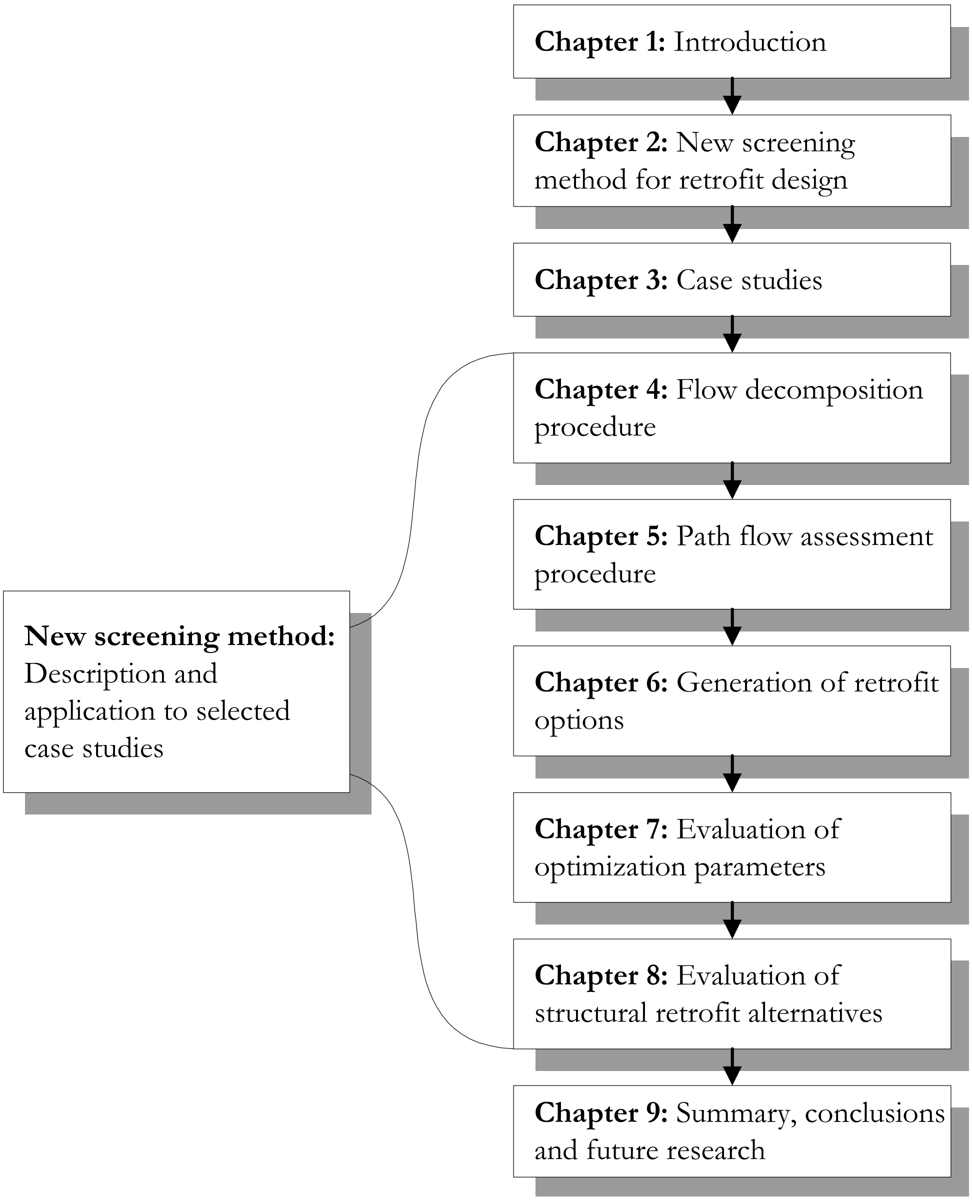


Figure 1-4: Outline of the thesis (see text for explanations)

2 NEW SCREENING METHOD FOR RETROFIT DESIGN

2.1 Importance of retrofitting in chemical industry

Research on retrofit design accelerated in the 80's after the energy crisis in the previous decade. Early work concentrated on applications of heat integration methods to increase the energy efficiency of continuous process plants. A similar development with respect to environmental concerns explains why in recent years the emphasis in retrofitting has been the environment. This section analyzes the importance of retrofitting today.

In a survey the Chemical Manufacturers Association (CMA)**[10]** (as cited in Guinand (2001)**[25]**) estimated the sales of the U.S. chemical industry for the year 2000 at 489 billion US$. In 1999, the total capital expenditures of the U.S. chemical industry represented roughly 9% of the estimated total U.S. sales for the year 2000. The capital expenditures were distributed into five categories as shown in Figure 2-1:

- Plants and equipment
- Research and development
- Health and safety
- Environmental protection
- Hazardous waste site clean-up and remediation

In 1999, the expenditures amounted to 53.9% for plants and equipment, 27.5% for research and development, 7.8% for health and safety, 6.6% for environmental protection, and 4.2% for hazardous waste site clean-up and remediation. Moreover, the survey also identified the capital expenditure distribution to different project types in the plant and equipment category (see Figure 2-1). The project types were:

- Capacity expansions (of existing production plants)
- Plant maintenance (replacement of worn-out equipment)

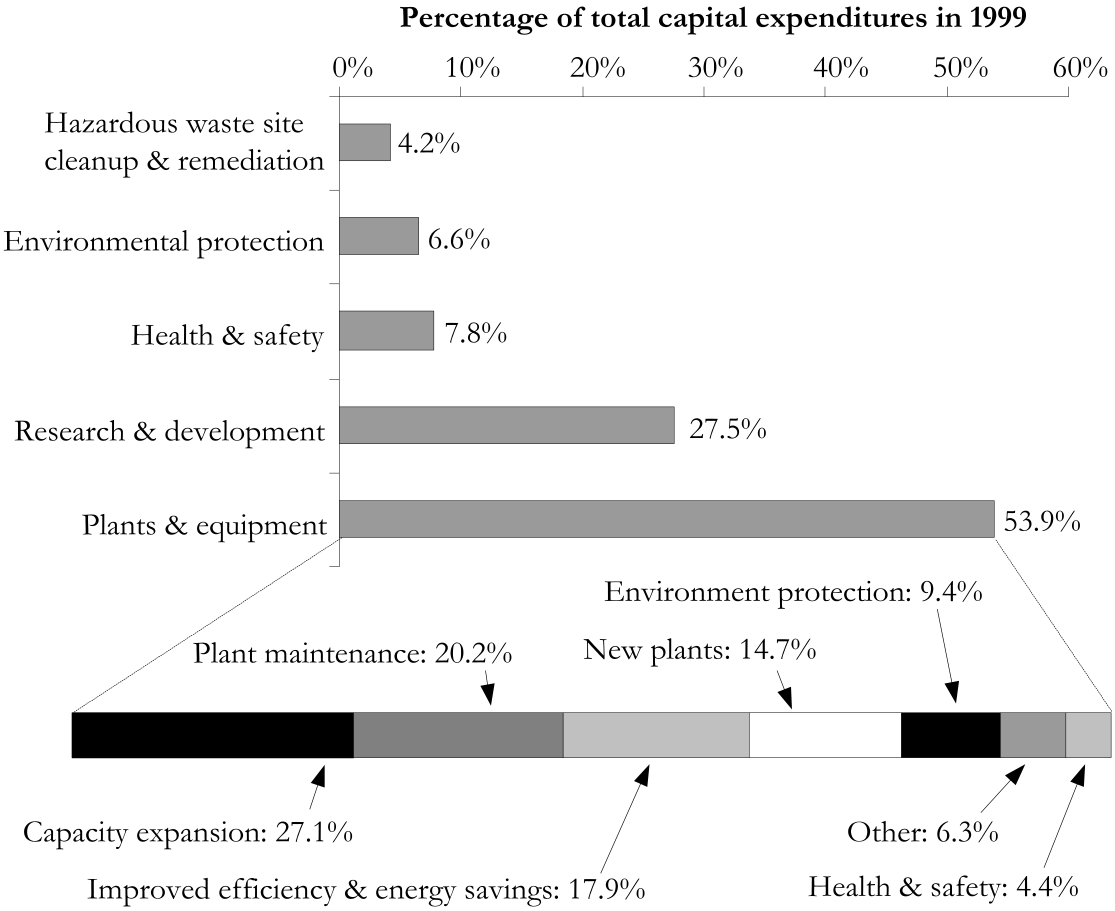


Figure 2-1: Capital investment of the U.S. chemical industry as percentage of total investments in 1999 (adapted from CMA (1999)[10] as cited by Guinand (2001)[25])

- Improvement of production cost efficiency (raw material and energy efficiency)
- New production plants
- Environmental protection
- Health and safety
- Other projects

Amazingly, only 14.7% of the capital expenditures in the plant and equipment category accounted for the construction of new production plants – the only non-retrofit category. Higher capital investments were spent for projects on capacity expansions, plant maintenance, and improvements of production cost efficiency.

From the results of this survey it can be concluded that 85.3% of the capital expenditures of the U.S. chemical industry for plants and equipment were directed to retrofitting. Based on the sales estimate for the year 2000, retrofitting therefore accounted for capital expenditures in the order of 37.5 billion US$. However, it should be noted that U.S. pharmaceutical companies were underrepresented in this market survey which probably led to slightly biased results. Further, it can be expected that a similar survey for the Swiss chemical industry would most probably yield different results since the Swiss chemical industry almost exclusively manufactures pharmaceuticals and fine chemical products. Nevertheless, the order of magnitude of the capital expenditures in the U.S. chemical industry clearly demonstrates the importance of retrofitting.

2.2 Comparison of grassroot and retrofit design

The number of methods that have been suggested for grassroot design is abundant. A good classification scheme for grassroot design methods was previously introduced by Gundersen (1989)**[26]**. Grassroot design methods comprise knowledge-based systems (expert systems – artificial intelligence), design methods based on heuristic rules, optimization methods stemming from operations research, and pinch methods (see Figure 2-2). The methods can be characterized as rather qualitative or quantitative and rather interactive or automatized. Some prominent early examples in these categories were introduced by Kirkwood et al. (1988)**[36]** (expert system), Douglas (1985)**[12]** (heuristic design method), Kocis and Grossmann (1989)**[37]** (MINLP optimization of process flowsheets), and Linnhoff et al. (1982)**[47]** (pinch technology for minimization of energy-use) based on earlier work by Linnhoff and Flower (1978)**[46]**.

All grassroot design methods that target the complete design of a process flowsheet follow to a certain degree a hierarchical procedure. At the first level the reaction system – if present – needs to be optimized, at the second level the separation system to purify the desired products and to recycle valuable reactants is conceived, at the third level an optimum heat exchanger network is

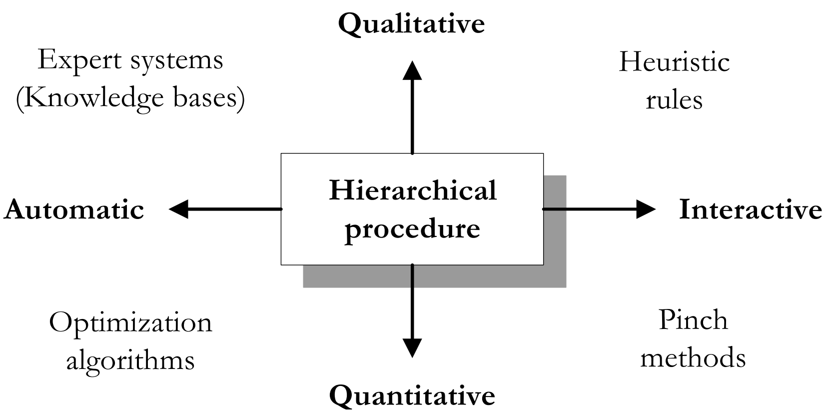


Figure 2-2: Characteristics of grassroot design methods

devised, and at the last level the required utility systems are determined. Iterations between the different levels are necessary in all methods.

Retrofit problems are often analyzed and evaluated with tools that were specifically developed for grassroot design. However, there are a few fundamental differences between the two design approaches:

- **Retrofitting is highly plant-specific:** Solutions to a retrofit problem are most often pre-determined to a certain degree by the historical evolution of the structure of the process plant. As a result a solution has to be individually "tailored" to the investigated process plant.
- **Retrofitting is driven by constraints:** In conjunction with the previous point, a number of important constraints limit the search space for solutions as e.g. limited space availability, specific infrastructure (e.g. availability of different types of utilities) of the site or the location in which the process plant is operated, and high maintenance costs among others. As already discussed in the previous chapter, the degrees of freedom in early phases of grassroot design are much higher than in retrofit design. Besides, investment into new equipment is capital intensive and often leads to unprofitable retrofit projects. In some cases a process retrofit alternative proves to be suitable with respect to technical feasibility and the aforementioned constraints, but in the end has to be rejected because of too high investments. Had the same alternative been considered before the plant was built, it would have been integrated into the original layout

of the plant. A good example of such a situation is reported by Guntern (1999)[27].

- **Retrofit implementation is a challenge:** The implementation of a solution to a retrofit problem has to be coordinated in a manner that minimizes the impact on plant operations (Cabano (1987)[8]). Different implementation strategies are in order of preference:

  [1] **Implementation in the plant without impact on production capacity and minor impact on plant operations:** This can be done e.g. by installing and testing of new equipment in the plant while the plant is operating, then by connecting the new equipment to the plant in a minimum of time when the plant is not required to operate at maximum production capacity, and then by compensating the resulting production losses afterwards.

  [2] **Implementation during the routine maintenance shut-down:** This might lead to a longer process down-time and possibly incur production losses.

  [3] **Implementation during a non-routine shut-down:** By consequence, there is a fair chance that the yearly production capacity might not be met since production losses result from this strategy.

  Additionally, information on the changes in operating conditions after retrofitting might have to be gathered and extrapolated from tests runs in the plant, prior to the planned plant modifications.

- **The combinatorial size of the evaluation problem:** The solution of a retrofit problem requires the evaluation of a larger number of alternatives as compared to grassroot problems (Grossmann et al. (1987)[24]). This is due to the fact that not only process retrofit alternatives have to be evaluated but also that the reuse of existing equipment has to be considered since economics dictate the reuse of existing equipment as much as possible. Existing equipment might however be required to operate far from its design conditions. Therefore, both the evaluation of process retrofit alternatives and the rating of existing equipment under different operating conditions needs to be undertaken in search of a solution to the retrofit problem. It is difficult to treat both tasks independently from each other as can be easily done in grassroot design (hierarchical procedure).

- **Retrofitting requires different mathematical tools:** Different mathematical tools are needed to rate existing equipment as compared to grassroot design. The so-called *rating models* are much more complex models than *design models* which are typically used in grassroot design. Rating models contain algorithms e.g. that check the capacity limitations of a defined piece of equipment or that calculate mass and energy exchange based on kinetic models instead of thermodynamic equilibrium models (e.g. distillation). These models are much more data intensive than design models. However, since the equipment is operated in the plant, much more information is available than is known during the development of a new process.
- **Experience in plant operations is available:** The experience in operating the investigated plant is a source of important information for retrofit design. These insights can be used to reduce considerably the combinatorial size of the retrofit problem. Experience can be transformed into specific heuristic rules and can help to quickly rate process retrofit alternatives.

2.3 Literature review on current retrofit design methods

2.3.1 Classification of current retrofit design methods

In the literature on retrofit design two distinctively different approaches to solving retrofit problems can be found: (1) the *practice-based* approach and (2) the *system-based* approach. Both approaches have their advantages and weaknesses but are complementary to each other. In the 80's most of the reported retrofit design methods were still rather based on only one of the two aforementioned approaches. In more recent times, retrofit design methods were introduced that combine the advantages of both approaches and thus try to eliminate their inherent weaknesses. In the following, both approaches are defined and described in more detail:

[1] **The practice-based approach:** Daily experience in plant operations, historic know-how in specific process technologies although better technologies might be available, an "equipment"-centered view as opposed to a "process"-centered view, and little time availability are factors that influence this approach. *Heuristic methods* represent methods that are based on this approach and are very similar to the heuristic and pinch methods used for grassroot design. These methods usually start from a base case of the investigated process and modify it by following a defined procedure in which e.g. heuristic rules of process engineering or physico-chemical insights of the process are used to take decisions at each level.

[2] **The system-based approach:** Research on retrofit design is rather focused on the overall process and tends to simplify and idealize a system in order to be able to apply various mathematical tools to analyze and evaluate a given problem. The system-based approach is often time-consuming and can be unaware of best operational practice and can thus make the development of a solution for a retrofit problem and its implementation slow. *Algorithmic* and *thermodynamic methods* are based on this approach. As in grassroot design, algorithmic methods typically make use of structural optimization strategies to analyze, evaluate and select the best possible process alternative for a given retrofit problem. Because often a large number of process retrofit alterantives have to be evaluated these methods require a good pre-selection of alternatives to ensure the feasibility of structural optimization. Thermodynamic methods were developed after the introduction of pinch technology (Linnhoff and Flower (1978)**[46]**).

The purpose of the following review is to introduce the most important existing retrofit design methods classified by the type of retrofit incentive they pursue in chronological order. The methods that address the problem of retrofit design in a broad context are described in more detail and discussed accordingly. Retrofit design methods can be found that target the improvement of the cost-efficiency of a process plant (including methods that purely aim at energy savings), seek to minimize process wastes, aim at increasing the production capacity of a plant, and try to improve the operational flexibility of a process. For future comparison, only the methods that share common elements with the new screening method introduced in this thesis are explained in more detail here.

2.3.2 Methods for improving the production cost efficiency

Most reported retrofit design methods concentrate on improving the production cost efficiency of a continuous process for the production of a single product. These can be divided into two sub-groups: (i) Methods that target energy savings by reducing the overall utility consumption of the process and (ii) methods that aim to improve the overall cost-efficiency of the process with regard to the variable production costs (raw materials, utilities, waste disposal).

Methods that target energy savings

A number of methods have been proposed for retrofitting the heat exchanger network (HEN) of a continuous process. These can be classified into two different categories. The first category comprises the retrofit design methods that use the concept of pinch technology. As previously stated, pinch technology was first introduced by Linnhoff and Flower (1978)**[46]** to design optimal heat exchanger networks and was later extended by Linnhoff et al. (1982)**[47]** for the minimization of energy-use in the design of entire processes (including the HEN). Tjoe and Linnhoff (1986)**[62]** then presented a method that adapts the latter method to the specific context of retrofit design. The second category comprises methods that deal with mathematical programming techniques and important contributions were made by Jones et al. (1986)**[35]**, Saboo et al. (1986)**[56]** and Ciric and Floudas (1989)**[9]**. During that time the development in the two categories evolved separately with little interaction between them. A later approach (Zhu and Asante (1999)[66]) combined the advantages of both types of approaches by using pinch technology in order to generate promising HEN designs and finding the best solution with optimization strategies.

A similar solution strategy, that was exploited in the work of Zhu and Asante, was also adopted by Kovac and Glavic (1995)[40] and Kovac-Kralj et al. (2000)[41] but extended to the retrofitting of entire processes (not only the HEN) with respect to energy consumption. The method undergoes two main steps. In the first step, process retrofit alternatives are generated by combining heuristics and pinch technology. In the second step, a superstructure that includes the generated alternatives is formulated and the optimal retrofit determined by simultaneous structural and parameter optimization (MINLP optimization).

Finally, Fraser and Hallale (2000)[20] presented a method that targets the retrofitting of mass exchange networks (MENs – can include all types of unit-operations where mass exchange occurs as e.g. absorption, extraction) for energy savings. El-Halwagi and Manousiouthakis (1989)[15] previously used the analogy between heat and mass transfer to apply pinch technology to the generation of MENs in grassroot design. Fraser and Hallale extended this analogy to retrofit design on the basis of the work of Tjoe and Linnhoff (1986)[62].

Methods for improving the overall cost efficiency

One of the most elaborated retrofit design methods of the past was presented by Fisher et al. (1987) based on earlier work by Fisher et al. (1985)[17] and is therefore described in more detail. It combines sensitivity analysis with elements of the hierarchically structured and heuristically-driven method for grassroot design introduced by Douglas (1985)[12]. Sensitivity analysis is used to vary operating parameters of the process with respect to the overall production costs (referred to as *total operating costs* by Fisher et al.) and to establish an *operating cost diagram*. The method includes the following steps:

[1] In a first step, the operating cost diagram for the existing process is used to identify the incentive for raw material and energy savings.

[2] The heuristic grassroot design method of Douglas (1985)**[12]** is then used to design new structural alternatives for the complete process as if the existing plant were to be completely replaced.

[3] Further, the new process alternatives are evaluated with the help of the operating cost diagrams and the best process alternative determined with a quick screening method.

[4] Based on the comparison of the existing process with the best process alternative the most important operating parameters are identified, studied in a sensitivity analysis and constraining equipment in the existing plant identified. The economically optimal sizes for new equipment are then determined by trading-off necessary investments with cost savings. Finally, heat integration using pinch analysis is performed.

The work by Fisher et al. (1987)**[18]** was partially automated and further extended by Nelson and Douglas (1990)**[50]**. It can be concluded that this method tackles the problem of improving the production cost-efficiency from a broad perspective in an efficient manner. However, the main drawbacks of this method are the use of simple models (accuracy of predictions uncertain), short-cut cost calculations and the comparison with the best process alternative which can lead to high investment costs for modifications of the existing process.

Lately, another broad approach to retrofit design was proposed by Guinand (2001)**[25]**. Guinand structured the approach in the following steps: formulation of retrofit incentive(s), process analysis, generation of retrofit alternatives for the structural modification of the process, and selection of the best retrofit alternative(s):

[1] **Formulation of retrofit incentive(s):** In this step, retrofit incentives are determined on the basis of a rigorous simulation model that represents a typical operating state of the investigated process (base case). A

variation of process operating parameters is performed with sensitivity analysis with respect to appropriate performance measures for a given retrofit incentive (e.g. improvement of cost-efficiency, flexibility). Guinand proposes this concept to determine the most important retrofit incentives, however only the incentive of improving the cost-efficiency of a process is studied in detail. Starting from the results of the sensitvity analysis a parameter optimization is then carried out to minimize the variable process costs.

[2] **Process analysis:** The optimized process is transformed using *graph representation* in order to visualize and calculate the flow of each process component on its different trajectories (also referred to as *paths*) in the process (*open* trajectories and *closed* trajectories, if recycling occurs in the process). Process raw material and energy costs are then allocated to the different component flow trajectories based on their molar flowrates.

[3] **Generation of structural retrofit alternatives:** The component flow trajectories and their allocated costs are approximated as a linear process model and studied by sensitivity analysis. Structural retrofit alternatives are then generated from the results of this analysis.

[4] **Selection of the best retrofit alternative(s):** Finally, based on the findings of the previous step, the best structural retrofit alternatives are represented in a *superstructure* either by modification of the linear process model in [3] or by modification of the rigorous model in [1]. The best retrofit alternative(s) are then determined by optimizing the superstructure using simultaneous parametric and structural optimization (*MINLP* optimization).

It can be concluded that Guinand's method puts retrofit design into the widest frame so far. The method analyzes a given process for key "problems" that could be improved by retrofit design. After a small number of promising retrofit alternatives have been generated in step [3] and represented in a superstructure, the method relies on MINLP optimization techniques in order to identify the best retrofit alternative(s) in [4]. This pre-selection of structural retrofit alternatives can reduce the complexity of the MINLP problem, yet does no guarantee a solution due to the inherent difficulties associated with MINLP optimization. A drawback of Guinand's method is that the procedure is relatively time-consuming because of multiple sensitivity analyses and optimizations. Besides, the issue of actually generating structural retrofit alternatives from the sensitivity results in [3] is sparsely treated and would require further elaboration.

2.3.3 Methods for waste minimization

Due to increased environmental awareness and regulations in the 80's, as already mentioned in Chapter 1, the emphasis in grassroot design shifted from end-of-pipe technologies to the reduction of waste and the reuse of waste as most cost-effective waste management methods. This development led to the definition of preferences in waste treatment (hazardous/non-hazardous) by the U.S. Environmental Protection Agency (EPA):

[1] Reduction at the source (e.g. by good operating practices, technology changes, input material changes, or even product changes)

[2] Recycling (e.g. recycling of wastes to the original process, use as a raw material substitute for another process, external recycling for resource recovery (reclamation))

[3] Treatment with end-of-pipe technologies (e.g. waste incineration facilities, waste-water treatment plants)

Source reduction is generally accepted as the best waste handling procedure (Stephan and Atcheson (1989)[59]) for two main reasons: (i) the emissions to the environment are reduced by not even generating them in the first place; (ii) reduced waste generation directly reduces expensive end-of-pipe waste treatment costs and often reduces energy costs in production and in waste treatment.

A number of retrofit design methods that tackle the problem of waste minimization in existing processes have been reported in literature. Douglas (1992)[14] modified his hierarchically-structured and heuristic-driven approach for the design of new processes (Douglas (1985)[12]) to include the objective of waste minimization. This change consists in an adapted set of heuristic rules to make decisions on waste handling at the various levels of the hierarchical procedure. Douglas' statement, that the method originally developed for grass-root design can also be applied to retrofit design of processes, was later validated by Fonyo et al. (1994)[19] by application to several case studies.

Later, two different approaches to perform retrofit design for waste minimization were proposed by Van der Helm and High (1996)[64] and Dantus and High (1996)[11]. Both approaches are structured in a procedure that includes three main steps: base case modelling of the existing process in a flowsheet simulator, identification of process retrofit alternatives on the basis of a case-specific study of the process (not generalizable), and optimization with regard to economic performance while minimizing waste by source reduction. In the former approach, only the most relevant process operating parameters are optimized, while in the latter additional structural process retrofit alternatives are generated which are then evaluated by simultaneous parameter and structural optimization techniques (MINLP optimization). A crucial point of these approaches is the joint minimization of waste generation at the source under economic considerations.

Most recently, a new retrofit design method for waste minimization has been introduced by Halim and Srinivasan ((2002a,b)[29][30]). An expert-system is used to visualize the flow of materials in continuous processes in an abstracted manner using graph representation, however less developed than presented in the work of Guinand (2001)[25]. In an interactive procedure, waste sources and variables that are reponsible for generating wastes in the different unit-operations are identified, and process retrofit alternatives are generated by the use of heuristic rules. It can be concluded that this method primarily aims to assist the decision-maker in analyzing the process and generating promising process retrofit alternatives from a waste minimization perspective.

2.3.4 Methods for increasing production capacity

Although capacity expansion was identified in Section 2.2 as the most important retrofit incentive in terms of capital expenditure, very few retrofit design methods that approach this aspect of retrofit design are reported in literature. Rapoport et al. (1994)**[55]** presented a method that mainly aims at expanding the production capacity of a plant but also targets retrofit incentives to use new raw materials. The method consists of an interactive algorithm that is based on heuristics rules and is organized in a hierarchical procedure. Moreover, tools for the design of equipment and for the calculation of capital costs are used to evaluate the generated process retrofit alternatives. Later, Ben-Guang et al. (2000)**[4]** proposed another systematic procedure to deal with increasing production capacity in continuous processes. However, the procedure is only intended as a conceptual guide to efficient project management with regard to retrofitting for capacity expansion since at each step of the method the applied strategies are formulated in a rather general context.

2.3.5 Methods for improving flexibility

Continuous processes are constantly influenced by varying input parameters and external disturbances (e.g. varying feed-rates from other plants, extreme variations of the outside temperature). Most of these uncertainties are handled by the process control system. However, variations in operating conditions cannot be completely prevented. Therefore, processes have to exhibit a certain degree of operational flexibility to encompass sudden changes in operating conditions. A retrofit design method that focuses on improving the flexibility in plant operations was presented by Pistikopoulos and Grossmann (1988)**[52]**, (1989a,b)**[53][54]**. This method makes use of a flexibility index (Swaney and Grossmann (1985)**[60]**, Grossmann and Floudas (1987)**[23]**) that defines the maximum allowable variation range of uncertain parameters in order to maintain operations. Given a pre-defined index value of flexibility, the method minimizes the capital costs related to process modifications in order to achieve the desired value.

2.4 Limitations of current retrofit design methods

In this section, the main limitations of current retrofit design methods are addressed and used to summarize the desired attributes for new retrofit design methods. Perhaps one of the most important limitations of current retrofit design methods – with the exception of the conceptual idea presented by Guinand (2001)[25] – is that there is as yet no unified, systematic strategy for dealing with retrofit problems. The greatest progress has been made in the fields of energy savings and waste minimization, followed by approaches that aim at improving the production cost efficiency of a process. Today the aspect of capacity expansion has only been treated sparsely. Further limitations are:

- Most of the presented methods do not recognize important differences between grassroot and retrofit design. Especially the importance of rating the equipment for use under different operating conditions either by plant experience or by calculation is often not paid enough attention to in the analysis and evaluation of process retrofit alternatives.
- The experience gathered during the life-time of the plant is generally not taken into account. Although some methods are based on heuristic rules, these have been derived from a grassroot design perspective and do not reflect on the available specific process-knowledge.
- Especially the algorithmic types of methods that make use of simultaneous parameter and structural optimization are in principle suited for the automatic evaluation of a defined set of process retrofit alternatives. However, due to the great complexity of such combined optimization techniques, simple models have often to be used to represent equipment. Moreover, these methods have been mostly applied to relatively simple and idealized processes.

- Judging from a time perspective only few methods lead to results in a short time frame. Current practice in chemical industry however demonstrates the importance of the time factor. Economics dictates a quick response to external and internal conditions (see Section 1.2) in order to preserve competitiveness on the market.
- In current retrofit design not all retrofitting strategies (repiping, modification of existing equipment, replacement of existing equipment, and addition of new equipment – see Section 1.2) are addressed, i.e. only the replacement of existing equipment or the addition of new equipment are considered.
- One aspect that almost all of the methods presented above fail to recognize is that decisions in retrofit design are not solely based on evaluation results. In daily practice, knowledge of an attractive solution of a retrofit problem is not sufficient if this knowledge cannot be transferred to other team-members or even to the decision-maker. Therefore, the different methodological steps of a retrofit design method should be practicable, transparent, systematic, objective, and easily communicable in order to increase the chances of acceptance in daily routine.

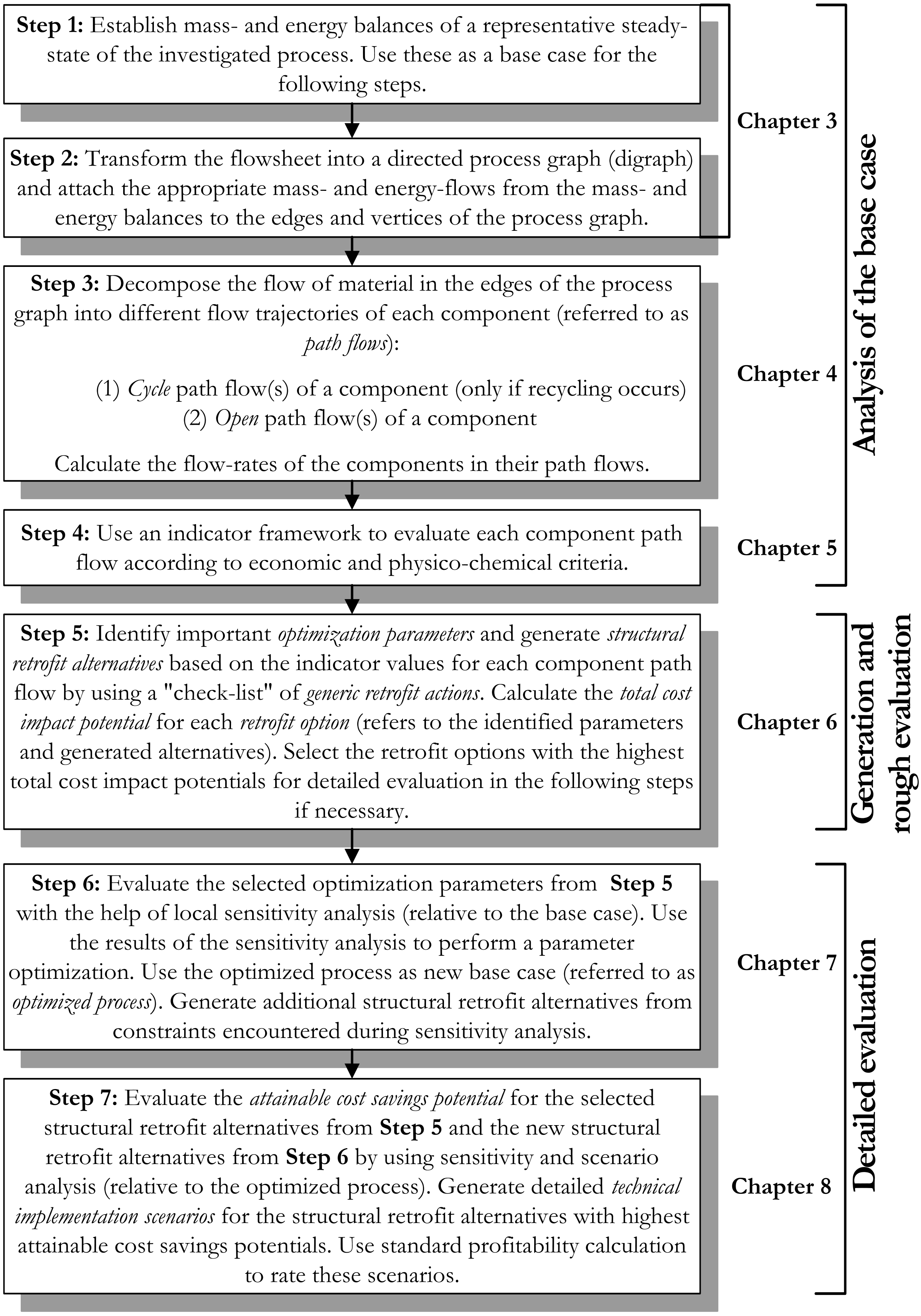
From these findings it can be summarized that an ideal retrofit design method should be capable of addressing retrofit problems with respect to multiple incentives and multiple performance measures (such as economics and environmental impact). Further, a method should take advantage of process-specific knowledge, reveal insights of the process to increase the understanding, be practicable in a short time frame, communicable, systematic, objective, and transparent. An ideal retrofit design method should also take all retrofitting strategies (repiping, modification of existing equipment, replacement of existing equipment, and addition of new equipment – see Section 1.2), as mentioned, into account and should generate retrofit alternatives that comply with important criteria such as process safety, controllability, and operability. Lastly, future methods should include the possibility to rate equipment on a detailed basis when needed and should be applicable to a wide range of processes.

2.5 Description of the new screening method

In this section, a rough overview of the proposed screening method is given. This method is specifically aimed at the improvement of production cost-efficiency in continuous processes.

The review on current retrofit design methods highlights two general principles in approaching a retrofit problem: the practice-based and the system-based approach. It is almost obvious that a good retrofit design method, in order to take advantage of these complementary approaches, has to include elements of both approaches in a sensible manner. In view of the combinatorial problem size when faced with systematically generating process retrofit alternatives the alternative generation step should be decoupled from the decision step for the best alternative(s). The practice-based approach shows clear advantages for the pre-selection of promising retrofit alternatives since operational knowledge, specific process-knowledge, and known process-constraints can act as efficient filters. The other approach on the other hand (especially optimization techniques) is well suited for the decision process when only few alternatives remain. Further, as mentioned in the thesis statement in Section 1.4, a thorough analysis of the base case design with respect to the selected retrofit incentive and an appropriate performance measure can potentially help to focus only on the relevant "chances and problems". The screening method proposed in this thesis is therefore structured in three phases (see Figure 2-3):

[1] **Analysis of the base case:** First, and foremost it is assumed that the decision-maker knows the external and internal conditions (see Section 1.3) and has defined a retrofit incentive in response to the changed conditions. In this thesis only the incentive of improving the production cost-efficiency of a process is studied. In **Step 1**, the base case design is established by either measuring mass and energy balances in the existing plant or by simulation. The former is preferable as the simulation of a complex plant can be tedious and time-consuming. In **Step 2**, the flowsheet of the investigated process is represented as a process graph which is only needed to prepare **Step 3**. The analysis



Step 1: Establish mass- and energy balances of a representative steady-state of the investigated process. Use these as a base case for the following steps.

Step 2: Transform the flowsheet into a directed process graph (digraph) and attach the appropriate mass- and energy-flows from the mass- and energy balances to the edges and vertices of the process graph.

Step 3: Decompose the flow of material in the edges of the process graph into different flow trajectories of each component (referred to as *path flows*):

(1) *Cycle* path flow(s) of a component (only if recycling occurs)
(2) *Open* path flow(s) of a component

Calculate the flow-rates of the components in their path flows.

Step 4: Use an indicator framework to evaluate each component path flow according to economic and physico-chemical criteria.

Step 5: Identify important *optimization parameters* and generate *structural retrofit alternatives* based on the indicator values for each component path flow by using a "check-list" of *generic retrofit actions*. Calculate the *total cost impact potential* for each *retrofit option* (refers to the identified parameters and generated alternatives). Select the retrofit options with the highest total cost impact potentials for detailed evaluation in the following steps if necessary.

Step 6: Evaluate the selected optimization parameters from **Step 5** with the help of local sensitivity analysis (relative to the base case). Use the results of the sensitivity analysis to perform a parameter optimization. Use the optimized process as new base case (referred to as *optimized process*). Generate additional structural retrofit alternatives from constraints encountered during sensitivity analysis.

Step 7: Evaluate the *attainable cost savings potential* for the selected structural retrofit alternatives from **Step 5** and the new structural retrofit alternatives from **Step 6** by using sensitivity and scenario analysis (relative to the optimized process). Generate detailed *technical implementation scenarios* for the structural retrofit alternatives with highest attainable cost savings potentials. Use standard profitability calculation to rate these scenarios.

Figure 2-3: Structure of the new screening method (explanations are provided in the text)

procedure actually starts at this step by decomposing the flowsheet streams into flow trajectories of single components along an *open path* or a *cycle path*, if recycling occurs in the process. Open path flows of a component originate either in an external feed or by reaction in a vertex and are terminated either in a process output or by consumption in a reaction. Cycle path flows instead are an idealized representation of the specific flow-rate of a component that circulates endlessly inside the process. Based on the flow-rates of components in open and cycle path flows, variable process costs are allocated to each component path flow from a raw material cost as well as an energy and waste cost perspective in **Step 4**. Two physico-chemical indicators have been developed and are also used to rate the non-ideality of a component path flow inside the process.

[2] **Generation and rough evaluation of retrofit options:** This phase is the most difficult aspect of the screening method and is undertaken in **Step 5**. The central idea consists in a simultaneous identification of important process operating parameters (referred to as *optimization parameters*) and generation of promising structural modifications to the plant (referred to as *structural retrofit alternatives*). The results from the analysis level are studied with a list of generic actions (*generic retrofit actions*) and *retrofit options* (optimization parameters and structural retrofit alternatives) are generated for each component path flow that exhibits economic improvement potential. The retrofit options are then screened (rough evaluation) with regard to their economic impact potential. The screening value (*total cost impact potential*) serves as a performance measure to rank the retrofit options among each other and can be used to select the most promising options in the interest of time.

[3] **Detailed evaluation of the identified retrofit options:** The last phase of the screening method comprises two evaluation steps (**Steps 6** and **7**) to refine the selection of promising retrofit options. In

Step 6, the identified optimization parameters are further studied with pre-optimality sensitivity analysis and optimized accordingly. The *optimized process* serves as a new reference case in **Step 7**. If an optimization parameter hits a process constraint in the sensitivity analysis but still indicates an important cost sensitivity at the bound, this information is exploited to define new structural retrofit alternatives in addition to the alternatives resulting from **Step 5**. Finally, **Step 7** introduces a two level approach for final selection among the structural retrofit alternatives. The first level evaluates the attainable cost savings with each alternative again through the use of sensitivity analysis. The most important retrofit alternatives are then selected in the second level and *technical implementation scenarios* (solutions for the retrofit problem) are formulated. Prior to profitability analysis each technical implementation scenario needs to be optimized (parameter optimization since the structural decision variables are fixed). Compliance with numerous criteria such as safety, operability, and others can then be checked and a profitability calculation carried out.

The method is applied to two industrial case studies: (i) the hydro-dealkylation process of toluene to manufacture benzene (*HDA case study*) and (ii) the production of a fine chemical (*Fine Chemical case study*) as an example of a complex plant. The screening for the HDA process is performed only up to **Step 5** and the resulting retrofit options compared to the retrofit options reported in literature. The Fine Chemical process is studied with the complete screening method and the resulting retrofit options compared with current efforts in retrofit design on-site.

The proposed screening method includes a number of elements found in the two broadest approaches that address production cost-efficiency in retrofit design (Fisher et al. (1987)**[18]**, Guinand (2001)**[25]**). Sensitivity analysis is used by Fisher et al. (1987)**[18]** and by Guinand (2001)**[25]** in the analysis phase of their methods in order to identify retrofit incentives and important optimization parameters. In contrast, the presented method makes use of sensitivity analysis only in a later phase (phase [3]) in order to evaluate optimization parameters and structural retrofit alternatives that were identified to be of major importance in phase [2].

The approach of Fisher et al. relies on heuristic rules and a quick cost screening procedure for generating structural retrofit alternatives. Guinand's method makes use of graph representation to decompose the process flowsheet into open and cycle path flows of each component in a process and allocates process raw material and energy costs to these path flows. In principle, the presented screening method combines elements of both approaches. A similar flow decomposition procedure as reported by Guinand is used. However, the proposed cost allocation to the resulting component path flows is more refined and two additional physico-chemical performance indicators are used in order to gain more information from the process. The list of generic retrofit actions in fact comprises heuristic rules and supports the identification of important optimization parameters and structural retrofit alternatives simultaneously. The impact potential of each retrofit alternative on the variable costs of the investigated process is also intended for quick screening purposes and follows a similar line of thought as proposed by Fisher and his co-workers.

Finally, in contrast to Guinand's approach that identifies the best structural retrofit alternatives by MINLP optimization, the presented method avoids the complexities associated with simultaneous parametric and structural optimization. Instead, attainable cost savings for each generated structural retrofit alternative in **Steps 5** and **6** are calculated using sensitivity analysis in **Step 7**. Technical implementation scenarios (detailed modifications of the flowsheet topology) are only generated for the structural retrofit alternatives with the highest attainable cost savings. These can then be evaluated by more simple parameter optimization.

The main advantages of the proposed screening method are the relatively short time-frame in which the first analysis and generation phases of the method can be performed if detailed mass and energy balances are available. However, in the evaluation phase there is no other way to assess the generated retrofit options in more detail than by using rigorous simulation, sensitivity analysis and optimization. Another advantage resides in combining heuristics with the systematic analysis procedure based on a component path flow perspective instead of a unit-operation-based perspective. Further, the evaluation of a selected number of technical implementation scenarios at the end can potentially accelerate the decision process, since detailed rating of equipment is kept minimal. Although considerable support is given in this method to the decision-maker about generating structural retrofit alternatives, the systematic generation of structural retrofit alternatives with respect to the four retrofitting strategies mentioned in Section 1.2 still remains a procedure solely driven by process insights and general engineering knowledge.

3 CASE STUDIES

3.1 Overview

Two case studies are chosen to demonstrate the presented screening method: (i) The toluene hydro-dealkylation process for the production of benzene (HDA case study) which has been extensively used in chemical engineering literature; (ii) a process for the production of an organic intermediate needed in the fine chemical industry (Fine Chemical case study). A detailed process description is given in Sections 3.4.1 (HDA case study) and 3.5.1 (Fine Chemical case study). For confidentiality reasons the names of the chemical components as well as specific process information involved in the Fine Chemical case study are not mentioned.

As shown in Figure 2-3 **Step 1** of the screening method requires the knowledge of the process main component mass balances as well as an energy balance at a characteristic steady-state operating point. Further, economic data for raw materials, utilities, waste disposal and products are required. Moreover, the process boundaries have to be clearly defined as complex connections between different processes are often encountered in production sites. The required mass and energy balances are determined for both case studies by process simulation (see Sections 3.4.2 and 3.5.2) using the commercial flowsheeting software Aspen Plus® (AspenTech (1998)[1]). Regarding the Fine Chemical case study, component mass balances were measured before the process was simulated and were used to fine-tune the simulation to match these as well as possible. Although older energy balances were also available, information on current operating parameters (e.g. reflux ratios in distillation columns) was used to generate the energy balances only by simulation.

Step 2 of the screening method requires the transformation of the process flowsheet into a process graph (*digraph* or *directed graph*) that contains the information of the previously determined mass and energy balances. The transformation procedure is described for both case studies in Sections 3.4.3 and 3.5.3.

An introduction to the principles of graph theory is given in the following section.

3.2 Introduction to graph theory

Graph theory can be used to represent systems composed of discrete objects and relationships among these objects (Mah (1990)[49]). The objects are generally referred to as *vertices* (synonyms are: nodes, points, or junctions) and the relationships as *edges* (synonyms are: arcs, lines, or branches). Graph representations are often used to visualize processing tasks in general and thus have been applied to represent continuous chemical processes. When relationships between two vertices have a direction (e.g. heat flows, material flows) those graphs are called *directed graphs* or *digraphs*. An example of a digraph for a simple process is illustrated in Figure 3-1.

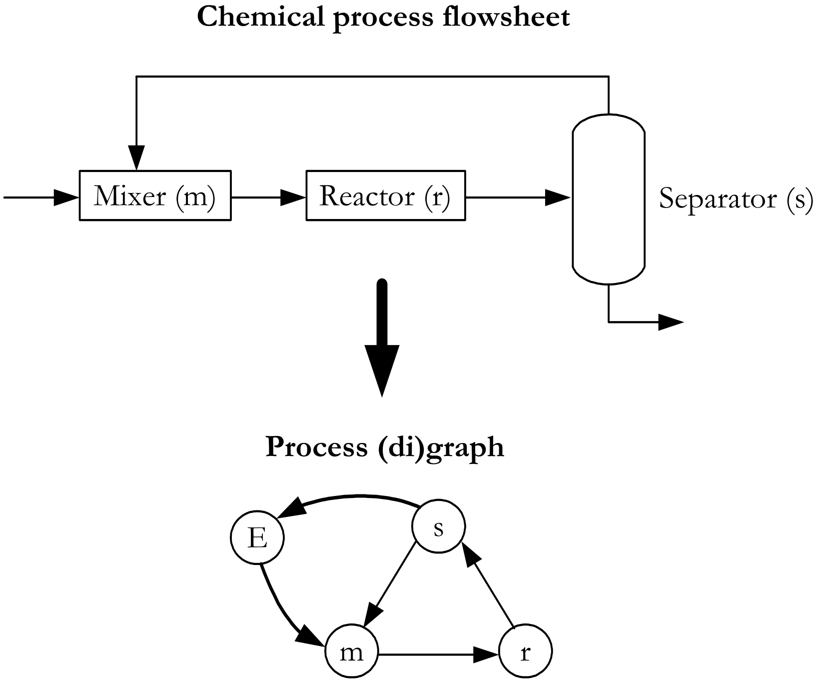


Figure 3-1: Transformation of a chemical process flowsheet into a process digraph (see text for explanations)

In Figure 3-1, vertex E refers to the environment (called *environment node*), i.e. the origin and destination of the feed to Mixer (m) and the bottom output of Separator (s). If two vertices (e.g. r and s) are linked by an edge, they are said to be *adjacent* to each other, edges that point to a vertex are called *positively incident* to that vertex, and edges that point away from a vertex are referred to as *negatively incident* to that vertex. Vertices can represent abstract tasks (those graphs are referred to as *State-task networks (STN)*) or the equipment in which the tasks are carried out (referred to as *State-equipment networks (SEN)*). These modified graph representations were introduced by Kondili et al. (1993)**[39]**. In the task representation these authors differenciated between two types of tasks: (1) *One task-one equipment (OTOE)* and (2) *Variable task-equipment (VTE)*. In the latter representation multiple equipment with different tasks can be grouped together in a single vertex. When reactions occur in a process, reactants disappear and products are generated which can be visualized in STN-graph representations as shown in the example of Figure 3-2. The bold arrows pointing to the vertices (m) and (r) are referred to as *supply flows* (by external feed or generation in a reaction) and the other bold arrows as demand flows (by output or consumption in a reaction). Supply and demand flows can be either drawn for a single component or can contain the supply or demand flows of multiple components.

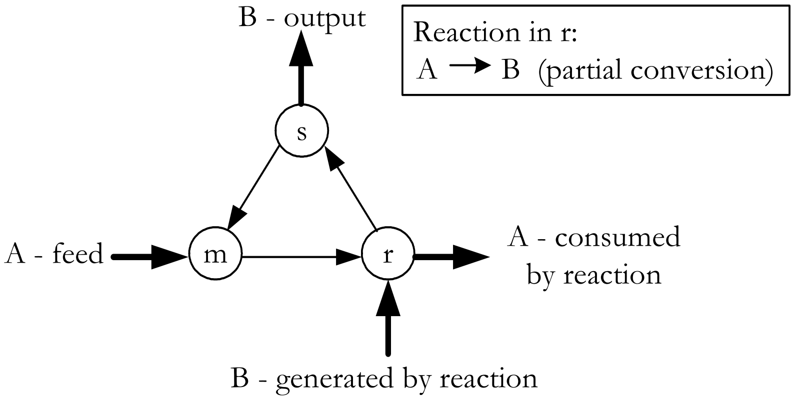


Figure 3-2: State-task representation with respect to chemical reactions (see text for explanations)

3.3 Introduction to steady-state process simulation

Process flowsheet simulators are used to represent the material and energy streams flowing in a chemical process plant. These programs are able to model the interconnected unit-operations of the process either in a dynamic or in a stationary state (steady-state). Process simulation is extensively used in process design of chemical process plants (Futterer and Munsch (1990)[22]). Typically, process flowsheet simulators contain two model types for unit-operations: *design* and *rating* models. The objective of design models is to determine the dimensions of the equipment in a particular configuration given a set of input components and the desired product specifications. In rating models the objective is to simulate an existing process and calculate output conditions when the equipment characteristics and input conditions are known.

Current process flowsheet simulators can be classified as *modular*, *equation-oriented*, or as a combination of both. In the equation-oriented mode, the process equations (unit, stream connectivity, and sometimes thermodynamic models) are assembled and solved simultaneously. In the modular mode, unit and thermodynamic models remain self-contained as sub-programs or procedures containing the unit-operation specific design equations. These are then called at a higher level in order to converge the stream connectivity equations represented in the flowsheet topology (Biegler et al. (1997)[5]).

Sequential modular process flowsheet simulators are comprised of model libraries representing unit-operations (Evans et al. (1979)[16]). The modeller builds a flowsheet in a graphic user interface from unit-operation building blocks while the process flowsheet simulator adds the corresponding sub-programs to each block. Moreover, the sub-programs require physical property data that is provided from a library of physical property models. The sub-programs are then solved in a sequence that roughly parallels the flow of material on the actual process. Instead, equation-oriented process flowsheet simulators solve unit-operation connectivity, unit-operation design equations, and physical property equations simultaneously.

3.4 HDA case study

3.4.1 HDA process description

Douglas (1988)[13] describes various flowsheet alternatives (separation section and plantwide heat integration alternatives) for the HDA process. Figure 3-3 shows the flowsheet of the process alternative selected in this thesis. This specific process alternative corresponds to the HDA alternative that Fisher et al. (1987)[18] used as a base case in their retrofit study and that Kocis and Grossmann (1989)[37] used as initial flowsheet in their MINLP-optimization. The main process operating parameters are also taken from the aforementioned publications so that the results obtained in this thesis can be compared with those reported in the two earlier studies. The most important process design and operating parameters are displayed in Table A-1 in the Appendix.

Fresh toluene (To) is fed to mixer M2 to which the liquid toluene distillate of column D3 is recycled. Both streams are pumped to the pressure required for reactor R with pumps P1 and P3. Fresh and already pre-pressurised hydrogen (H_2) with 5 vol% methane (CH_4) impurity at the desired pressure is then mixed to the toluene stream in mixer M1. Further, the recompressed gas recycle from compressor C, that mostly contains methane and hydrogen, is also added to the hydrogen/toluene mixture in M1. The resulting hydrogen/toluene/methane mixture is then partially evaporated in heat exchanger H2 and completely evaporated in fired heater H10 before the mixture enters the adiabatic reactor RK in which the exothermic main- and side-reactions to benzene (Bz), methane, diphenyl (Dp), and hydrogen occur:

$$\mathrm{To} + \mathrm{H_2} \rightarrow \mathrm{Bz} + \mathrm{CH_4} \qquad \textit{(REq. 3-1)}$$

$$\Delta H_{\mathrm{R}}^{621\,°\mathrm{C},\ 36\ \mathrm{bar}} = -49.5\ \mathrm{kJ/mol},\ X^{(To)} = 0.75$$

$$2\ \mathrm{Bz} \rightleftarrows \mathrm{Dp} + \mathrm{H_2} \qquad \textit{(REq. 3-2)}$$

$$\Delta H_{\mathrm{R}}^{621\,°\mathrm{C},\ 36\ \mathrm{bar}} = 13.0\ \mathrm{kJ/mol},\ S^{(Dp)} = 55$$

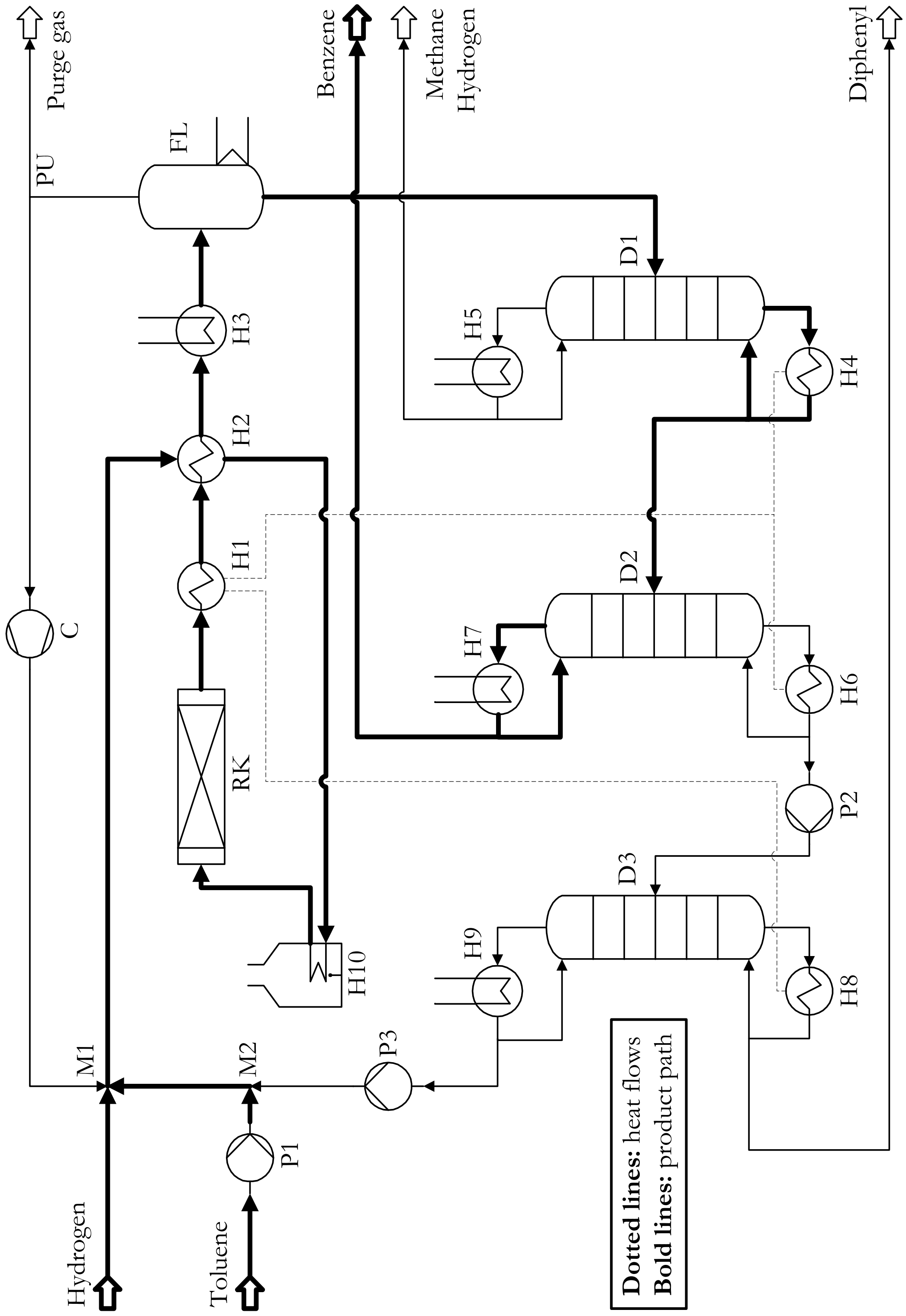


Figure 3-3: HDA process flowsheet: RK – HDA reactor with solid bed catalyst; D1 – stabilizing column; D2 – benzene distillation column; D3 – toluene distillation column; M1, M2 – mixers; C – recycle gas compressor; FL – flash drum; H1-H4-H6-H8 – process heat exchange network; H2 – process heat exchanger; H3 – water quench cooler; H5, H6, H9 – column conden-sers; H10 – natural gas fired heater; P1, P2, P3 – pumps; PU – purge split

Here ΔH_R represents the heat of reaction at the indicated temperature and pressure, $X^{(To)}$ represents the conversion with respect to toluene, and $S^{(Dp)}$ the selectivity of the formation of diphenyl (defined as the ratio of the benzene molar flow-rate to the diphenyl molar flow-rate leaving reactor RK).

After the RK reactor outlet is partially condensed (without the non-condensibles hydrogen and methane) in heat exchange network H1-H4-H6-H8 (process heat is used in the reboiler of the three distillation columns D1, D2, and D3) and in the aforementioned heat exchanger H2 it is further condensed by quenching in water cooler H3 and then flashed in flash-drum FL. The gas-phase that mostly contains the non-condensibles (hydrogen and methane) is then partially purged (PU), recompressed in compressor C, and finally recycled to mixer M1. The liquid-phase – containing essentially benzene, diphenyl, and toluene – is processed through stabilising distillation column D1 to remove the remaining non-condensibles, then through distillation column D2 to separate the desired product benzene, and finally through distillation column D3 to separate the by-product diphenyl from the remaining toluene. The recovered toluene with a low diphenyl-concentration is then again recycled to mixer M2.

3.4.2 HDA process simulation

The HDA process is modelled with the commercial flowsheet software package Aspen Plus® as a steady-state simulation. The design production capacity of the simulated HDA process plant is arbitrarily set to 100000 t/a. Further, a yearly operation time of 8000 h is assumed – therefore the simulation yields 12.5 t/h of benzene and is latter referred to as *base case model*. Detailed mass balances of the the base case are found in Table A-2 and the energy duties of the utility consuming unit-operations are shown in Table A-3 in the Appendix.

The distillation columns, including reboilers and condensers, in Figure 3-4 are calculated with the rigorous RADFRAC-model. The FL flash-drum is represented by a FLASH2-model. Water quench cooler H3 and fired heater H10 are calculated with the HEATER-model whereas heat exchanger H2 is represented by a HEATX-model. Pumps P1, P2, and P3 are all modelled with the PUMP-model. Finally, reactor RK is calculated as a RPLUG-model with kinetics for the main reaction *(REq. 3-1)* and the side reaction *(REq. 3-2)* taken from Luyben et al.[48]. The heat integration between process cooler H1 and the reboilers of the three distillation columns H4, H6, and H8 is included in the base case model (see Figure 3-4). The UNIQUAC-model is used to calculate the vapor-liquid equilibria (VLE-data) between all binary combinations of the components of the flowsheet and the necessary VLE-parameters taken from the internal Aspen Plus® databank. Any missing VLE-parameters for binary component pairs are calculated by the UNIFAC group-contribution method. The distillation columns are generally set up with individual component murphree efficiencies of approximately 0.7.

3.4.3 HDA process graph

The simplified directed process graph for the previously described HDA process flowsheet is shown in Figure 3-4. For simplification purposes, most of the vertices of the process graph combine multiple unit-operations. The fresh hydrogen and toluene feed, pumps P1 and P3, as well as mixers M1 and M2 are represented by vertex MI. The process heat exchange network H1-H4-H6-H8 is combined with process heat exchanger H2 because these heat exchangers require no further utilities. This group of units is symbolized by two vertices HX1 and HX2 in order to show that no mass exchange actually occurs. Fired heater H10 is then represented as a single vertex FH and reactor R as vertex RK. Water quench cooler H3 and flash-drum FL are joined in vertex FL. Compressor C is directly represented by vertex CO and purge-split PU by vertex PU. Finally, three distillation columns D1, D2, and D3 including their condensers H5, H7, and H9 are represented as vertices DS, DB, and DT, respectively.

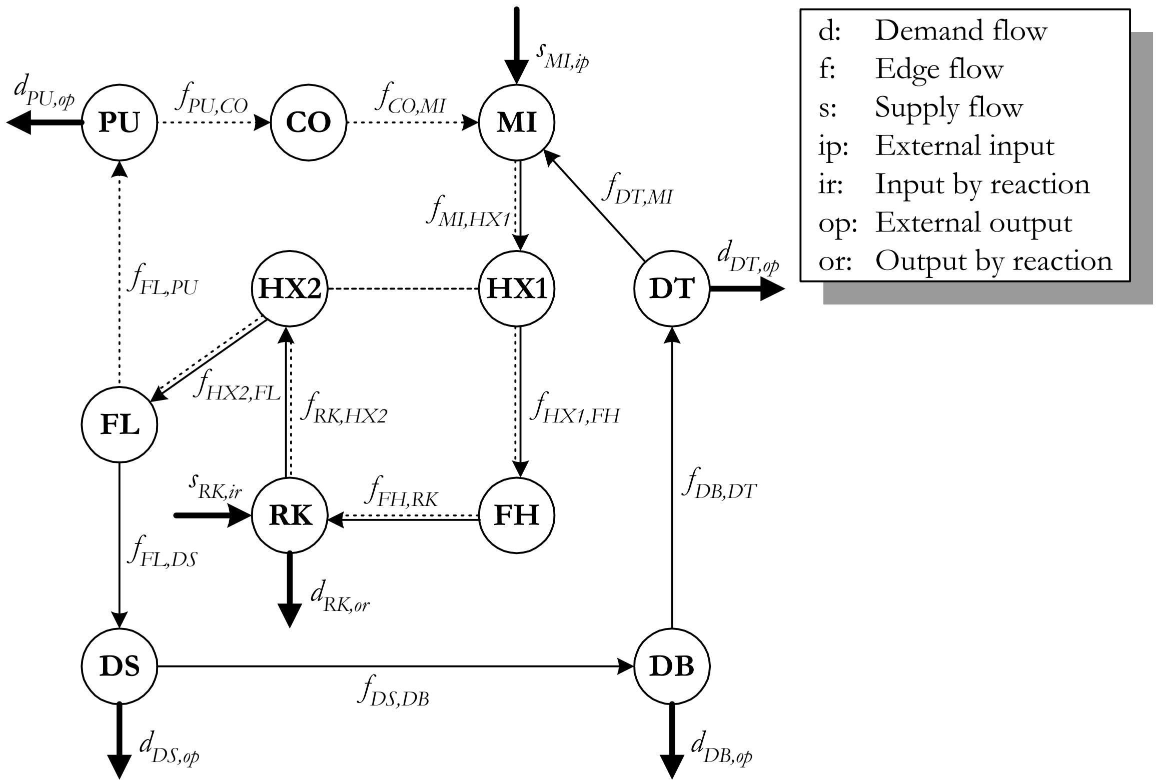


Figure 3-4: Process graph of the HDA case study (see text for abbreviations – dotted arrows: edge flows in the gas cycle; plain arrows: edge flows in the liquid cycle; dotted line between HX1 and HX2: heat flow; $s_{MI1,ip}$-MI1-HX1-FH-RK-HX2-FL-DS-DB-DT-$d_{EX,op}$: product path; bold arrows: supply and demand flows)

3.5 Fine Chemical case study

3.5.1 Fine Chemical process description

The process flowsheet for the manufacture of the Fine Chemical product is shown in Figure 3-5. Next to the main components (reactants R1 and R2, intermediate product I, coupled product CP, water, product P, and main by-product B) also approximately 30 different undesired impurity components circulate in the process either because they are fed from other production facilities to mixer M2 or because they are generated by the main components or by other impurities in reactors RK1 and RK2. In most cases the chemical structure is unknown as are the reactions by which they are generated. In order to circumvent this problem the impurities are collectively handled as impurity-groups. Each impurity is attributed to an impurity-group based on its observed

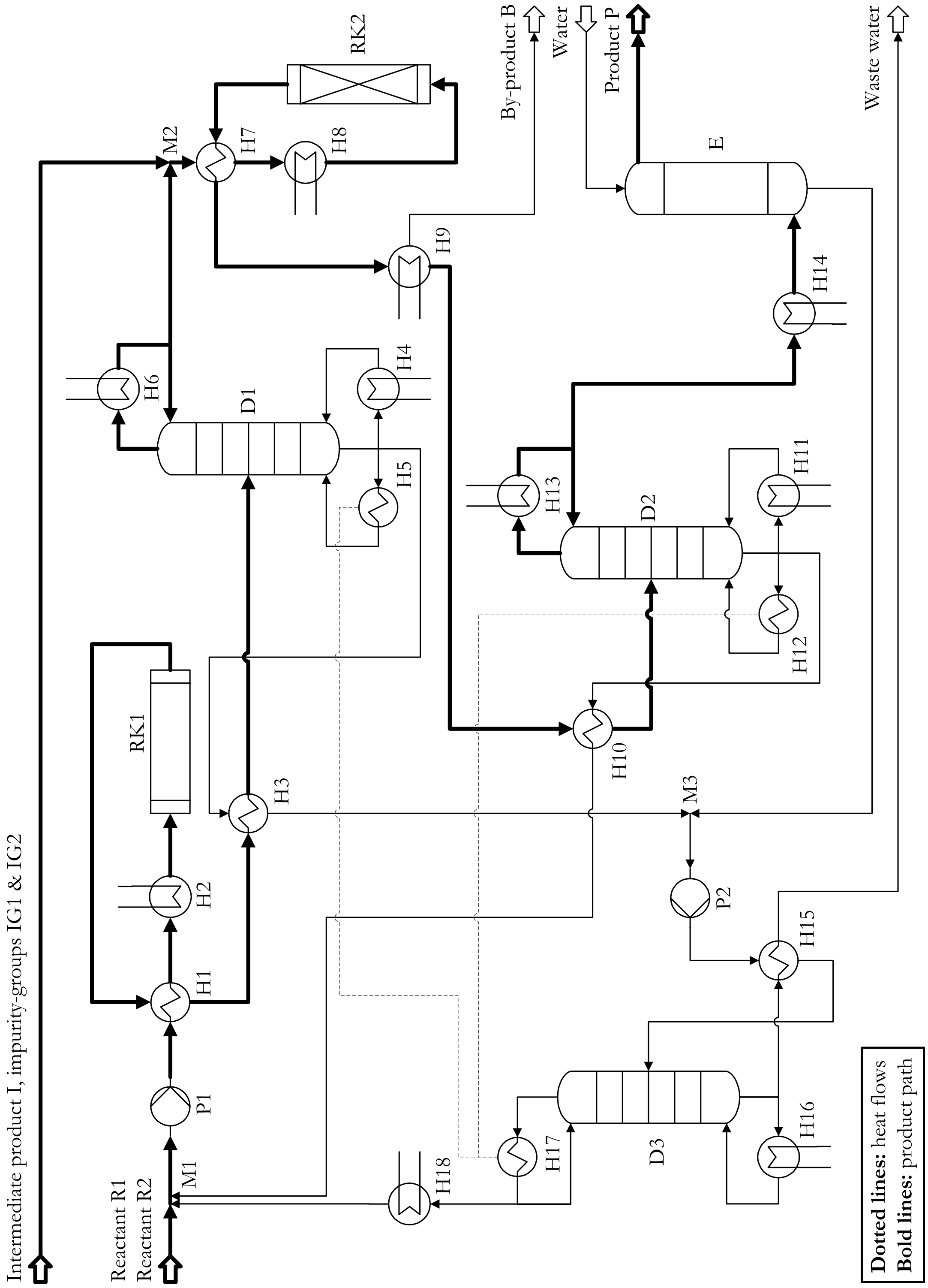


Figure 3-5: Fine Chemical process flowsheet: D1, D2, D3 – distillation columns; E – extractor for P product purification; H1, H3, H7, H10, H15 – process heat exchangers; H2, H9, H14 – coolers; H8 – heaters; H4, H11, H16 – column reboilers; H6, H13, H18 – column condensers; H5-H12-H17 – process heat exchange network; M1, M2, M3 – mixers or storage tanks; P1, P2 – pumps; RK1 – tubular reactor; RK2 – reactor with solid bed catalyst

flow pattern in the process and whether its retention time in a gas chromatograph in analysis using a standard non-polar separation column is shorter or longer than the retention time of the intermediate product I. Both criteria are chosen not only to simplify the discussion but also to simplify rigorous calculations in the simulations and is explained in more detail in Chapter 7. In turn, the simplification of course distorts the real picture but – given the available process data – is believed to be a good approximation. The impurities mostly accumulate in two cycles (first cycle: M1-RK1-D1-RK2-D2-M1, second cycle: M1-RK1-D1-M3-D3-M1) so that two impurity-groups IG1 (middle-boiling impurity-group) and IG2 (high-boiling impurity-group) are stipulated. Impurity-group IG1 mainly accumulates in the first cycle whereas impurity-group IG2 tends to accumulate in the second cycle. The impurity-groups are represented by two place-holder components that are similar to their corresponding impurities by chemical formula and by their flow pattern in the process.

Reactants R1 and R2 are fed to a storage tank represented by mixer M1 (Figure 3-5) to which mainly recovered reactant R2 from the distillate of column D3 is recycled. The liquid mixture is pumped to the desired pressure by pump P1, then pre-cooled by exchanging its process heat with the RK1 reactor outlet in heat exchanger H1, and further cooled down in a cooling system. The mixture is then fed to reactor RK1 where a first reaction step according to the reaction equation

$$\nu_{11}\mathrm{R1} + \nu_{12}\mathrm{R2} \rightleftarrows \nu_{13}\mathrm{I} + \nu_{14}\mathrm{CP} \qquad \textit{(REq. 3-3)}$$

occurs to an intermediate product I and a coupled product CP. The reactor output flows through the process heat exchangers H1 and H3 and is fed to distillation column D1 where coupled product CP is then removed from the process through the bottom product. Because reactant R2 acts as an intermediate key in the distillation the bottom product consists of a CP/R2-mixture. The distillate of the column contains all unconverted reactant R1 from the feed, the remaining reactant R2, and all of the generated intermediate product I. In mixer M2 additional intermediate product I from different production facilities enters the process along with low concentrations of the impurity-groups IG1 and IG2. The resulting mixture is heated to the required reaction temperature with process heat exchangers H7 as well as H8 and is partially converted to product P in the second reactor RK2 as follows:

$$\nu_{21}\mathrm{I} \rightarrow \nu_{22}\mathrm{P} + \nu_{23}\mathrm{R2} \qquad \textit{(REq. 3-4)}$$

After cooling in heat exchanger H9 the output of reactor RK2 is fed to distillation column D2 to pre-separate product P in the distillate from reactants R1 and R2. Since low concentrations of both reactants still remain in the distillate, P is finally cooled in heat exchanger H14 and purified in extractor E with water. The enriched water-phase (reactants R1 and R2) is then mixed with the bottom product of distillation column D1 in another storage tank, represented as mixer M3. The bottom product of distillation column D2 – mostly containing reactants R1 and R2 – is recycled to storage tank MI1. The content of storage tank M3 is pumped to a higher pressure and fed to distillation column D3 where coupled product CP steming from the first main reaction *(REq. 3-3)* and from the extraction is almost completely separated from reactant R2. The aqueous phase (contains almost all of the CP coupled product and low concentrations of R2) of the bottom product of distillation column D3 is then sent to a waste treatment plant. A high pressure is set in distillation column D3 so that a high percentage of the column overheads can be used to provide heat to the reboilers of distillation columns D1 and D2. The uncondensed overheads are completely condensed in heat exchanger H18 and then recycled to the storage tank M1.

Side-reactions also takes place in reactors RK1 and RK2. In reactor RK1, a small amount of recycled product P is almost completely converted back to reactants R1 and R2 according to the following reaction equation:

$$\nu_{31}\mathrm{P} + \nu_{32}\mathrm{CP} \rightarrow \nu_{33}\mathrm{R1} + \nu_{34}\mathrm{R2} \qquad \textit{(REq. 3-5)}$$

Detailed mass balances of reactor RK1 indicate that impurity-group IG2 is essentially generated by reactant R1. A “dummy” reaction equation is postulated to take these side-reactions into account:

$$\nu_{41}\mathrm{R1} \rightarrow \nu_{42}\mathrm{IG2} \qquad \textit{(REq. 3-6)}$$

This reaction equation is formulated in such a way that the molecular masses are equal on both sides of the equation. However, the atom balances are not fulfilled because the chemical formula of the place-holder component does not match the average chemical formula of all impurities in that impurity-group.

Multiple side-reactions occur in reactor RK2. The most important side-reaction is the known decomposition of the intermediate product I to reactant R1 and by-product B:

$$\nu_{51}\mathrm{I} \rightarrow \nu_{52}\mathrm{R1} + \nu_{53}\mathrm{B} \qquad \textit{(REq. 3-7)}$$

Similar reasons as described for reactor RK1 also yield two more “dummy” reaction equations in reactor RK2 in which impurity-group IG2 is decomposed to impurity-group IG1 or by-product B.

$$\nu_{61}\mathrm{IG2} \rightarrow \nu_{62}\mathrm{IG1} \qquad \textit{(REq. 3-8)}$$
$$\nu_{71}\mathrm{IG2} \rightarrow \nu_{72}\mathrm{B} \qquad \textit{(REq. 3-9)}$$

Again the reaction equations have equal molecular masses on both sides but do not fulfill their atom balances.

3.5.2 Fine Chemical process simulation

The Fine Chemical process is also modeled with the commercial flowsheet software package Aspen Plus® as a steady-state simulation. A base case which represents an average operating steady-state of the existing plant is simulated with a simulation model – latter referred to as *base case model* – on the basis of measured component mass balances in the existing plant. The accuracy of the base case model representation is highlighted in a comparison of the simulated and the measured component mass flows in Table A-4 in the Appendix. The energy balances, as already mentioned in Section 3.1, have been directly generated by simulation using available information on values of operating parameters (e.g. distillation column reflux ratios, column pressures).

In the base case model, the production flow-rate (see Figure 3-5) that contains >95 wt% of product P needs to correspond to a known market demand assumed to be fixed. Since R2 is the reactant used in excess (to increase the equilibrium conversion of reaction *(REq. 3-3)* in reactor RK1 of Figure 3-5) the reactant R1 feed-rate to the process controls the overall production flow-rate and is therefore fine-tuned to meet the desired production flow-rate.

The distillation columns, including reboilers and condensers, as well as the extractor of the process in Figure 3-5 are calculated with the rigorous RADFRAC-model. The heaters and coolers are calculated with the HEATER-model whereas the heat exchangers are represented by the HEATX-model. Finally, reactor RK1 is calculated as a CSTR-model with kinetics for the main reactions. The side-reactions *(REq. 3-5)* and *(REq. 3-6)* are described in a RSTOIC-model with constant fractional conversions based on the feed flow-rate of product P for *(REq. 3-5)* and of reactant R1 for *(REq. 3-6)*. Unfortunately, no reaction kinetics are available for the main reaction *(REq. 3-4)* in reactor RK2. Thus, the reactor can only be represented by a RSTOIC-model with a constant conversion and constant selectivities to the by-products of side reactions *(REq. 3-7)*, *(REq. 3-8)*, and *(REq. 3-9)*. The heat integration between the condenser of distillation column D3 and the reboilers of distillation columns D1 and D2 is not included in the base case model.

All site production facilities including the investigated Fine Chemical process plant generate organic wastes that are disposed of in an incineration facility to generate high pressure steam. The remaining heat energy in the combustion gases from the incineration facility is used to heat reactor RK2. Both energy credits are considered in the calculation of the variable costs (raw materials, electricity, waste disposal, cooling water, steam) for the base case model.

The UNIQUAC-model is used to calculate the vapor-liquid equilibria (VLE-data) between all binary combinations of the main components (reactant R1, reactant R2, intermediate product I, product P, coupled product CP, water) because the necessary VLE-parameters are either reported in literature or were determined through experiments beforehand. The VLE-parameters for the remaining binary combinations of the main components with the side components (by-product B, impurity-groups IG1 and IG2) and the side components among each other are either retrieved from literature or calculated by the UNIFAC group-contribution method. The distillation columns are generally set up with individual component murphree efficiencies of approximately 0.6 in the base case model in order to match approximately the measured process mass balances.

3.5.3 Fine Chemical process graph

The process graph of the described Fine Chemical process (compare Figure 3-5) is shown in Figure 3-6. The main storage tank for reactants R1 and R2 is represented by vertex MI1, while pump P1, process heat exchanger H1, cooler H2 and reactor RK1 are grouped together in vertex RK1. Further, process heat exchanger H3, distillation column D1, condenser H6, and column reboilers H4 and H5 are joined in vertex DI. Only mixer M2 is represented by vertex MI2, whereas process heat exchanger H7, heater H8, reactor RK2 and cooler H9 are considered as a reaction system and grouped together in vertex RK2. Moreover, process heat exchanger H10, distillation column D2, condenser H13, cooler H14, and column reboilers H11 and H12 are symbolized by vertex DP. The extractor E is represented by vertex EX and finally vertex DH references mixer M3, pump P2, process heat exchanger H15, distillation column D3, reboiler H16, and condensers H17 and H18.

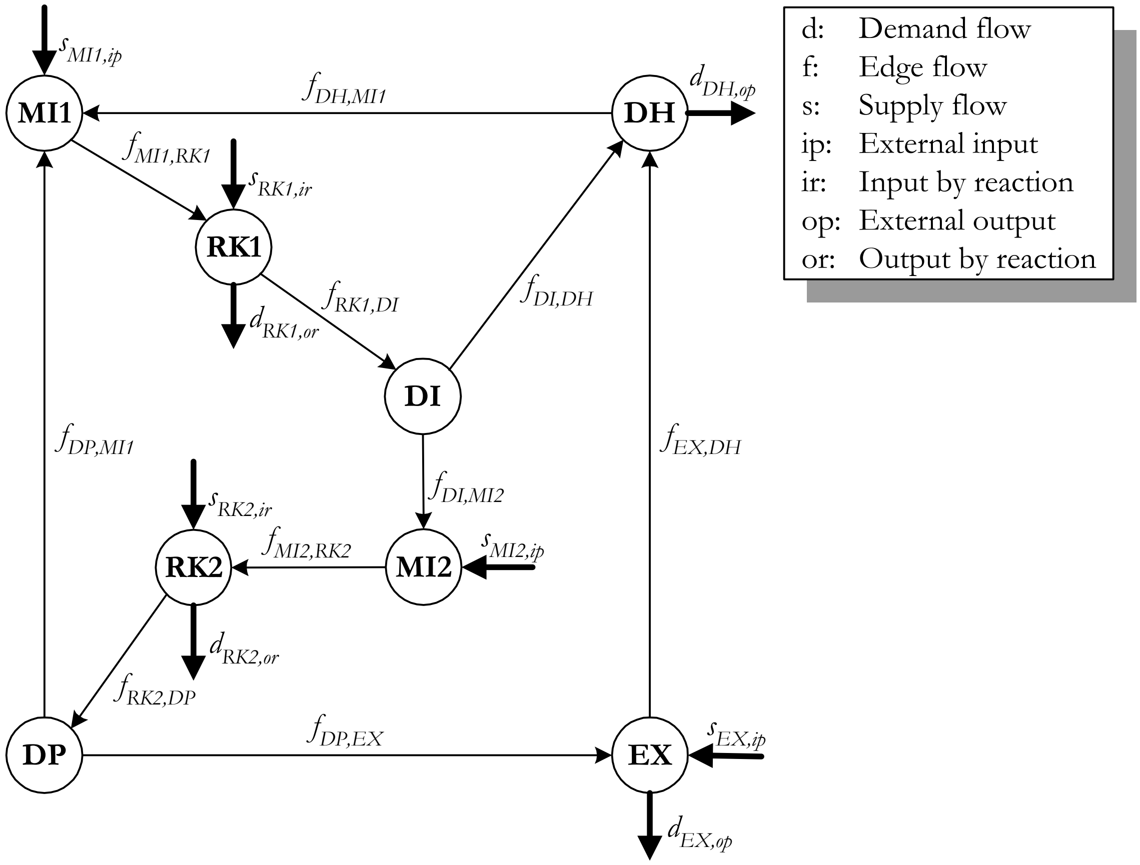


Figure 3-6: Process graph of the Fine Chemical case study (see text for abbreviations – bold arrows: supply and demand flows, plain arrows: edge flows)

4 FLOW DECOMPOSITION

4.1 Description of the flow decomposition procedure

In **Step 2** of the screening method a directed process graph that consists of a set of vertices (represent unit-operations or a sequence of unit-operations – see introduction to graph theory in Section 3.2) and edges (streams between these vertices) has been established and the information from the mass and energy balances have been attached to the process graph. In **Step 3** (see Figure 4-1) a decomposition technique derived from graph optimization theory is used to transform all edge flows of the process graph into path flows of the various components involved in the process. A process without recycles can be decomposed into open path flows. An open path flow of a single component consists of a trajectory from a vertex with supply flow (input/reaction) to a vertex with demand flow (output/reaction). If recycling occurs in the process, the flow decomposition technique additionally yields cycle (closed) path flows of a component that begin and end in the same vertex. The flow decomposition procedure consists of four steps:

4.1.1 Cycle paths in the process graph (Step 3-1)

If recycling occurs all cycles paths in the investigated process have to be identified before starting the path flow decomposition procedure. Sargent and Westerberg (1964) and later Tarjan (1972) introduced a general algorithm for the systematic identification of cycles (also referred to as *strongly connected components* in graph theory terminology) in process graphs. The algorithm consists in backtracking paths in a process graph until an already visited vertex is encountered for the second time - this procedure is repeated until all cycles are determined. All vertices participating in these cycles can thus be identified and formulated as a sub-graph of the complete process graph.

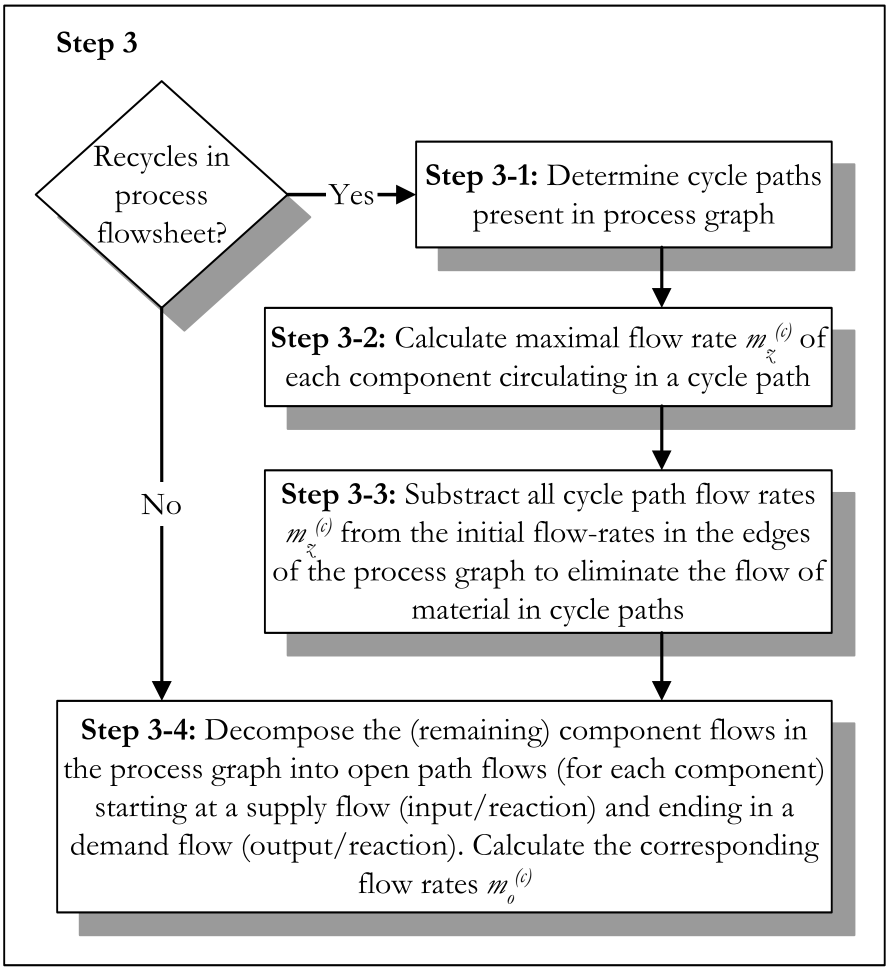


Figure 4-1: Principle of the flow decomposition procedure (see text for explanation of variables – Step 3 refers to the master scheme in Figure 2-3)

4.1.2 Maximum component flow-rates in cycle paths (Step 3-2)

As illustrated in Figure 4-2, mass balance equations are then established for each vertex of all cycle paths and each component flowing in the cycles of the sub-graph:

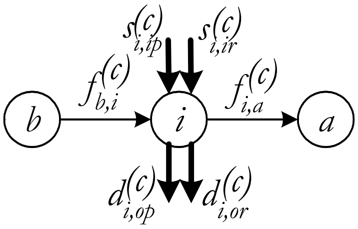


Figure 4-2: Schematic representation of the mass balance at a single vertex *i* (corresponding equations are given in *(Eq. 4-1)*, *(Eq. 4-2)* and *(Eq. 4-3)*)

$$\sum_{a=1}^{M} f_{i,a}^{(c)} - \sum_{b=1}^{N} f_{b,i}^{(c)} = d_i^{(c)} - s_i^{(c)} \qquad \text{(Eq. 4-1)}$$

$$d_i^{(c)} = \sum_{op=1}^{OP} d_{i,op}^{(c)} + \sum_{or=1}^{OR} d_{i,or}^{(c)} \qquad \text{(Eq. 4-2)}$$

$$s_i^{(c)} = \sum_{ip=1}^{IP} s_{i,ip}^{(c)} + \sum_{ir=1}^{IR} s_{i,ir}^{(c)} \qquad \text{(Eq. 4-3)}$$

$$\forall i \in SG, \forall c \in SC$$

in which $f_{i,a}^{(c)}$ and $f_{b,i}^{(c)}$ represent the flow-rates of component c in positively and negatively incident edges of vertex i, $s_{i,ip}^{(c)}$ and $s_{i,ir}^{(c)}$ are supply flow-rates that enter vertex i in a feed or are generated through reaction in i, respectively, $d_{i,op}^{(c)}$ and $d_{i,or}^{(c)}$ are demand flow-rates that either leave vertex i in a process output flow or are eliminated through reaction in i, respectively, $s_i^{(c)}$ and $d_i^{(c)}$ represent the sum of all supply flow-rates and all demand flow-rates of component c at vertex i, M and N are the number of positively and negatively incident edges of i, IP and OP are the number of process input and output flows in i, IR and OR are the number of supply and demand flows involved in reactions, SG is the set of vertices of the sub-graph, and SC is the set of components flowing through the sub-graph.

Further, the linear mass balance equations of all vertices of the sub-graph, as given in *(Eq. 4-1)*, can be represented in matrix notation:

$$\bar{B}^{(c)} \vec{f}^{(c)} = \vec{d}^{(c)} - \vec{s}^{(c)} \qquad \text{(Eq. 4-4)}$$

$\bar{B}^{(c)}$ denoting the edge-vertex incidence matrix that describes the aforementioned sub-graph (from **Step 3-1**) and $\vec{f}^{(c)}$ representing the vector containing the mass flow-rates of a single component in each edge of the complete process graph. The vectors $\vec{s}^{(c)}$ and $\vec{d}^{(c)}$ finally hold the total supply $s_i^{(c)}$ and demand $d_i^{(c)}$ mass flow-rates to each vertex of the sub-graph.

In order to calculate the maximum possible mass flow of a component in each cycle the following optimization problem can be formulated:

$$\max \sum_j y_j^{(c)} \tag*{(Eq. 4-5)}$$

$$\text{s.t. } \bar{B}^{(c)}[\mathrm{diag}(\vec{f}^{(c)})\vec{y}^{(c)}] = \vec{0} \tag*{(Eq. 4-6)}$$

$$\forall y_j^{(c)} \in (0;1)$$

Vector $\vec{y}^{(c)}$ contains mass flow fractions $y_j^{(c)}$ of each flow-rate in vector $\vec{f}^{(c)}$. The optimization problem simultaneously calculates for each cycle path its maximum possible cycle path flow-rate for a given component so that the constraints in *(Eq. 4-6)* are still fulfilled. Finally, these flow-rates can then be determined with the maximized $\vec{y}^{(c)}$ vector in the following manner:

$$\bar{D}^{(c)}\vec{x}^{(c)} = \mathrm{diag}(\vec{f}^{(c)})\vec{y}^{(c)} \tag*{(Eq. 4-7)}$$

where $\bar{D}^{(c)}$ represents the cycle-edge incidence matrix that attributes each edge of the sub-graph to one or more cycles. Vector $\vec{x}^{(c)}$ contains the maximum cycle path flow-rates for all cycles and can be calculated by solving *(Eq. 4-7)*. Although this equation-system will seem to be over-determined (more equations than cycles), it can be reduced to a linearly independent system of equations that contains the same number of equations as cycles in the sub-graph in which component *c* flows. This follows from two reasons:

a) A steady-state process with recycles necessarily yields a redundant equation-system *(Eq. 4-4)* for the sub-graph that comprises all vertices that are part of all cycles for a given component *c*.

b) The optimization problem *(Eq. 4-5)* and its constraints *(Eq. 4-6)* guarantee that there is only one maximized flow-rate for that component *c* in each cycle of the sub-graph because of the redundancy in a).

As there is only one maximized flow-rate for each component *c* in each cycle of the sub-graph and the equation-system is redundant, there can only be one linearly independent equation per cycle in equation-system *(Eq. 4-7)* for each component *c*. The dimension of vector $\vec{x}^{(c)}$ corresponds to the number of cycles present in the sub-graph. Therefore, there must be exactly the same number of linearly independent equations in equation-system *(Eq. 4-7)* as there are cycles in the sub-graph and thus the equation-system can yield only one solution. If there are more equations in this equation-system than the number of cycles, these have to be linearly dependent equations because of the redundancy of all equations in *(Eq. 4-4)*.

4.1.3 Elimination of the flow of components in cycle paths (Step 3-3)

Once the cycle path flow-rates have been calculated for each component and cycle path they are subtracted from the complete process graph. This procedure eliminates all component flows in cycle paths and leaves only open path flows in the now updated process graph.

4.1.4 Identification of open component path flows and their flow-rates (Step 3-4)

In the next step, flow distribution factors are established at each vertex of the complete process graph updated in **Step 3-3**. For processes in which no recycling occurs the flow decomposition procedure begins at this step. In process graphs with multiple supply and demand flows for one component a procedure for allocating a supply flow to the different demand flows has to be defined. Therefore, the assumption is made that ideal mixing occurs in each vertex. Thus, it is assumed that each flow entering a vertex leaves the vertex via the different exit flows with a probability proportional to their mass flow-rates. Thus, the flow distribution factors $w_i^{(c)}$ are defined for all flows leaving a vertex *i* (see Figure 4-2), e.g. demand flows *(Eq. 4-9)*, *(Eq. 4-10)*, and positively incident edges *(Eq. 4-11)*:

$$F_i^{(c)} = \sum_{b=1}^{N} f_{b,i}^{(c)} + \sum_{ip=1}^{IP} s_{i,ip}^{(c)} + \sum_{ir=1}^{IR} s_{i,ir}^{(c)} \qquad \text{(Eq. 4-8)}$$

$$w_{i,op}^{(c)} = \frac{d_{i,op}^{(c)}}{F_i^{(c)}} \qquad \text{(Eq. 4-9)}$$

$$w_{i,or}^{(c)} = \frac{d_{i,or}^{(c)}}{F_i^{(c)}} \qquad \text{(Eq. 4-10)}$$

$$w_{i,a}^{(c)} = \frac{f_{i,a}^{(c)}}{F_i^{(c)}} \qquad \text{(Eq. 4-11)}$$

In case $F_i^{(c)}$ is zero, all distribution factors in vertex *i* are automatically set to zero. The following algorithm describes this procedure:

Open path flow decomposition algorithm for component *c*:

[1] Select a supply flow $s_{i,ip}^{(c)}$ or $s_{i,ir}^{(c)}$ for component *c*.

[2] Choose either an edge $f_{i,a}^{(c)}$ or a demand flow ($d_{i,op}^{(c)}$ or $d_{i,or}^{(c)}$) leaving the vertex with component *c*. If a demand flow was chosen, go to [4], otherwise, continue.

[3] If an edge was chosen, follow the edge to the next vertex and repeat from [2] at the new vertex.

[4] Check if all possible flow trajectories (open path flows) from the selected supply flow of component *c* to all demand flows of component *c* have been determined in the complete process graph. If yes, continue. Otherwise, go to [2].

[5] Check if all supply flows have been selected. If not, select a new supply flow and repeat [1] to [4]. Otherwise, continue.

[6] Calculate the corresponding flow-rates for the entire open path flows determined through [1] to [5] by multiplication of the original supply flow-rates with all distribution factors that occur along their various path flows.

After application of the flow decomposition procedure to all relevant components *c* the complete process graph has been decomposed into open and cycle component path flows. The sum of all path flow-rates flowing through any edge yields the original flow in that edge prior to flow decomposition.

4.2 Flow decomposition example: Benzene in the HDA process

In this section the flow decomposition procedure described in the previous section is demonstrated using the HDA case study and the component benzene as an example. The flow decomposition is applied to both, the HDA case study and the Fine Chemical case study but overall results are only showed later in Chapter 6.

4.2.1 Benzene flow decomposition (Steps 3-1 to 3-4)

In the selected alternative of the HDA process (Figure 3-4) all vertices of the complete process graph are also part of the cycle-flow sub-graph. In this process alternative the hot reactor output is used to exchange heat with the reactor inlet in a heat exchanger network. As the two flows do not physically contact each other the heat exchanger(s) are therefore described as two separated vertices (HX1 and HX2). Thus, in **Step 3-1**, only two cycles are identified: (i) A gas cycle (small dotted arrows in Figure 3-4) and a liquid cycle (plain arrows in Figure 3-4) for which the incidence matrix $\bar{B}^{(Bz)}$ is formulated as:

$$\bar{B}^{(Bz)} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1 \\ -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 \end{bmatrix} \qquad \text{(Æq. 4-12)}$$

the rows and columns representing vertices and edges in the following order:

- Rows (top-to-down): MI, HX1, FH, RK, HX2, Fl, PU, CO, DS, DB, DT.
- Columns (left-to-right): $f_{MI,\,HX1}$, $f_{HX1,\,FH}$, $f_{FH,\,RK}$, $f_{RK,\,HX2}$, $f_{HX2,\,FL}$, $f_{FL,\,PU}$, $f_{PU,\,CO}$, $f_{CO,\,MI}$, $f_{FL,\,DS}$, $f_{DS,\,DB}$, $f_{DB,\,DT}$, $f_{DT,\,MI}$.

Along with the edge, supply and demand flow-rate vectors (units: kg/h)

$$\vec{f}^{(Bz)} = \begin{bmatrix} 868 \\ 868 \\ 868 \\ 13500 \\ 13500 \\ 866 \\ 742 \\ 742 \\ 12630 \\ 12620 \\ 126 \\ 126 \end{bmatrix}, \ \vec{s}^{(Bz)} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 12630 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \ \vec{d}^{(Bz)} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 124 \\ 0 \\ 9 \\ 0 \\ 12500 \end{bmatrix} \qquad \text{(Æqs. 4-13a-c)}$$

the mass-balance equation system is established in **Step 3-2** using *(Eq. 4-4)*.

The solution to the optimization problem – *(Eq. 4-5)* subject to the constraint *(Eq. 4-6)* – yields the vector containing the maximum edge flow-rates circulating in both cycles (units: kg/h):

$$\mathrm{diag}(\vec{f}^{(Bz)})\vec{y}^{(Bz)} = \mathrm{diag}\begin{bmatrix} 868 \\ 868 \\ 868 \\ 13500 \\ 13500 \\ 866 \\ 742 \\ 742 \\ 12630 \\ 12620 \\ 126 \\ 126 \end{bmatrix}\begin{bmatrix} 1 \\ 1 \\ 1 \\ 0.064 \\ 0.064 \\ 1.167 \\ 1 \\ 1 \\ 0.001 \\ 0.001 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 868 \\ 868 \\ 868 \\ 868 \\ 868 \\ 742 \\ 742 \\ 742 \\ 126 \\ 126 \\ 126 \\ 126 \end{bmatrix} \qquad \textit{(Eq. 4-14)}$$

Further the equation system *(Eq. 4-7)* is set up with the use of $\overline{D}^{(Bz)}$:

$$\overline{D}^{(Bz)} = \begin{bmatrix} 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 1 \\ 1 & 0 \\ 1 & 0 \\ 1 & 0 \\ 0 & 1 \\ 0 & 1 \\ 0 & 1 \\ 0 & 1 \end{bmatrix} \qquad \textit{(Eq. 4-15)}$$

Here the left column contains the edges in the gas cycle and right column contains the edges in the liquid cycle.

Even though the equation system seems over-determined as previously explained in section 4.1.2, the twelve equations are linearly dependent on only two equations so that the *(Eq. 4-7)* is in fact not over-determined and has a single solution $\hat{x}^{(Bz)}$ with the maximum cycle path flows:

- Gas cycle: 742 kg/h; liquid cycle: 126 kg/h.

In **Step 3-3** the cycle path flows are subtracted from the original edge flow-rates in the sub-graph and the flow distribution factors are calculated in **Step 3-4** (Table 4-1).

Table 4-1: Flow distribution factors for benzene in the HDA process

	$f_{MI,HX1}$	$f_{HX1,FH}$	$f_{FH,RK}$	$f_{RK,HX2}$	$f_{HX2,FL}$	$f_{FL,PU}$	$f_{PU,CO}$	$f_{CO,MI}$	$f_{FL,DS}$	$f_{DS,DB}$	$f_{DB,DT}$	$f_{DT,MI}$	$s_{RK,ir}$	$d_{PU,op}$	$d_{DS,op}$	$d_{DB,op}$
MI	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HX1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
FH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
RK	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
HX2	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
FL	0	0	0	0	0	0.0098	0	0	0.9902	0	0	0	0	0	0	0
PU	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DS	0	0	0	0	0	0	0	0	0	0.99925	0	0	0	0	0.00075	0
DB	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1
DT	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Finally, Table 4-2 shows the results of the complete decomposition procedure for benzene.

Table 4-2: Mass flow-rates obtained for benzene after flow decomposition

k	**Benzene path flow**	$m_k^{(Bz)}$, **[kg/h]**
1	Gas cycle (dotted path in Figure 3-4)	742
2	Liquid cycle (plain path in Figure 3-4)	126
3	$s_{RK,\,ir} - f_{RK,\,HX2} - f_{HX2,\,FL} - f_{FL,\,DS} - f_{DS,\,DB} - d_{DB,\,op}$	12500
4	$s_{RK,\,ir} - f_{RK,\,HX2} - f_{HX2,\,FL} - f_{FL,\,DS} - d_{DS,\,op}$	9
5	$s_{RK,\,ir} - f_{RK,\,HX2} - f_{HX2,\,FL} - f_{FL,\,PU} - d_{PU,\,op}$	124

4.3 Discussion and conclusions

The flow decomposition procedure yields open and cycle path flows for all components involved in the investigated process (cycle path flows only if recycling occurs in the process). The decomposition approach is intended to simplify the subsequent procedure of generating alternatives in case a complex process is to be investigated. In principle, a complex problem (process flowsheet) is deliberately decomposed into a set of simpler sub-problems (component path flows) that can then be screened individually with more ease for possible retrofit potentials.

However, the downside of this approach is that the existing physico-chemical interactions between the component path flows are neglected. In fact, the distinction between open and cycle path flows of the same component is an idealization since they are usually connected to each other in the investigated process. Further, the component path flows of different components can also influence each other (*example:* two open path flows of different components flowing through a heat exchanger could exhibit a non-neglectable heat of mixing which only occurs between these two components).

Another important topic to discuss is the decomposition procedure itself. As already mentioned in the previous paragraph, open and cycle path flows of the same component are an idealized picture of the flow pattern of that component. Yet, there is no unique approach to decompose the flow pattern of a single component into open and cycle path flows as indicated in similar research work by Guinand (2001)**[25]**. If a single supply flow and multiple demand flows of a component exist in a process graph, clearly each demand flow of that component has to originate from the only supply flow. However, components with multiple supply and demand flows can aggregate and re-distribute among the demand flows. Therefore, in the latter case assumptions have to be made in which manner the open component path flows are to be determined. In this thesis the following two basic assumptions are made:

- If multiple flows (supply or edge flows) of the same component enter a given vertex in a process graph, these mix in an ideal fashion.
- Based on the ideal mixing assumption each exit flow from that component leaves the vertex with a probability proportional to its mass flowrate.

Of course, the ideal mixing assumption is not always fulfilled, but is believed to be a reasonable assumption for a probabilistic distribution of each supply flow to each demand flow. Guinand (2001)[25] handles the single supply/multiple demand problem in the exact same manner as described in Section 4.1.4, while he proposes to solve the multiple supply/multiple demand problem in a different manner. His decomposition approach postulates a “preferred path” criterion which consists in a hierarchy of preferences for possible flow trajectories (paths) between multiple supply and demand flows.

5 COMPONENT PATH FLOW ASSESSMENT

5.1 Description of the path flow assessment procedure

Cycle and open path flows from **Step 3** of the screening method (see Figure 2-3) are assessed in **Step 4** with a set of indicators that quantitatively or qualitatively assess their performance within the process. The presented set of indicators is especially focused on maximizing economic efficiency. However, the modularity of the approach allows for additional indicators to be integrated for other retrofit goals. Figure 5-1 gives an overview of the assessment procedure. The different indicators are discussed in the following.

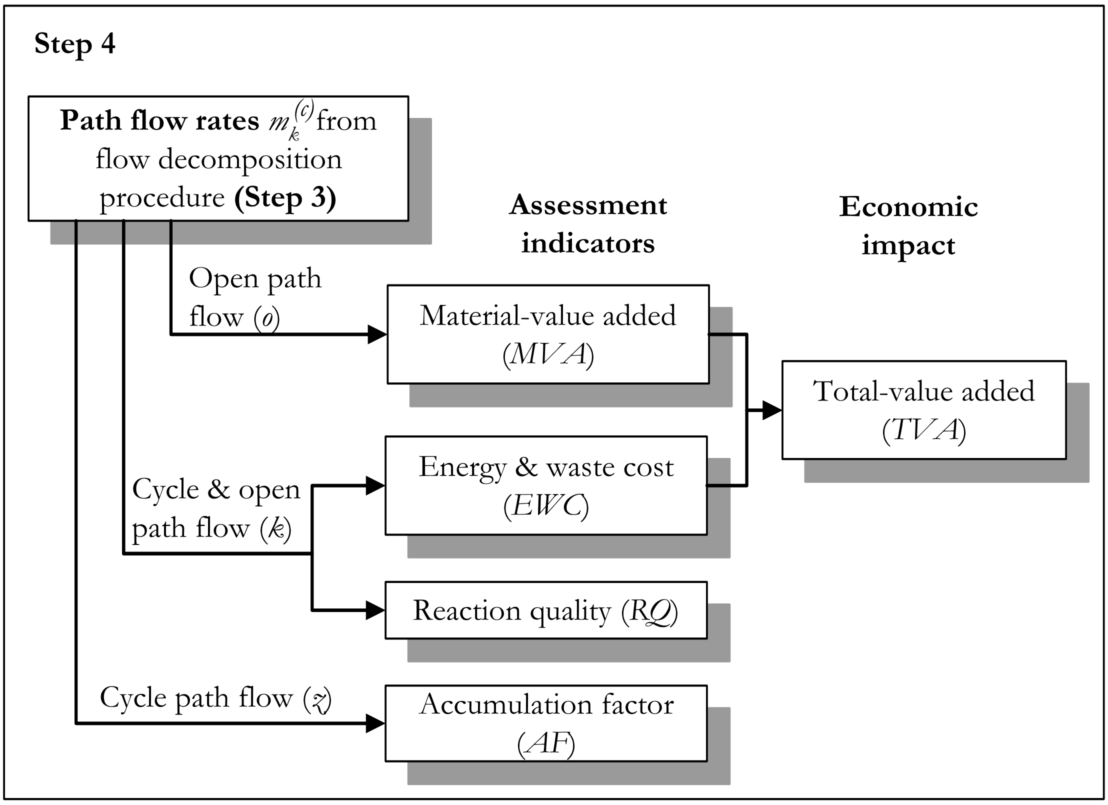


Figure 5-1: Structure of the path flow assessment procedure (see text for explanation of variables – Step 4 refers to the master scheme in Figure 2-3)

5.1.1 Material-value added (MVA)

The MVA-indicator is only applicable to open component path flows leaving the process boundaries in demand flows $d_{i,\,op}^{(c)}$ (see Figure 4-2) and calculates the difference between the value they represent outside the process boundaries and the costs in raw material consumption they caused (e.g. solvent: fuel credit in incineration - solvent purchase cost):

$$MVA_o^{(c)} = m_o^{(c)}\left(PP_o^{(c)} - PR_o^{(c)}\right) \tag*{(Eq. 5-1)}$$

in which $m_o^{(c)}$, $PP_o^{(c)}$, and $PR_o^{(c)}$ represent respectively the flow-rate of component *c* in open path flow *o*, the specific value outside the process boundaries (e.g. fuel credit or sales price), and the purchase price. Negative *MVA*-values indicate undesired value losses and hence highlight potentials for improvement on economic efficiency. In order to calculate *MVA*-values *(Eq. 5-1)* is used for open path flows of components that are externally fed to the process via supply flows $s_{i,\,ip}^{(c)}$ (Figure 4-2). The remaining open path flows necessarily originate in reaction supply flows $s_{i,\,ir}^{(c)}$ (Figure 4-2).

Before *MVA*-values can be calculated for these open path flows, *overall reaction equations* have to be formulated for the corresponding components starting from the process raw materials (only if multiple reaction steps are involved). In analogy to *(Eq. 5-1)* the equivalent purchase value for a component generated in the process is determined by its raw material consumption calculated with the help of the molecular weights $M^{(rm)}$ of the raw materials, stoichiometric coefficients $\nu^{(rm)}$ from the overall reaction equation, and purchase prices $PR^{(rm)}$:

$$MVA_o^{(c)} = m_o^{(c)}\left(PP_o^{(c)} - CA_o^{(c)}\left(\sum_{rm\,=\,1}^{RM}\frac{\left|\nu_o^{(rm)}\right|M_o^{(rm)}}{\nu_o^{(c)}M_o^{(c)}}PR_o^{(rm)}\right)\right) \tag*{(Eq. 5-2)}$$

where *rm* denotes the raw material index and *RM* the total number of raw materials involved in the overall reaction equation. As often multiple products are generated in an overall reaction equation, it becomes necessary to allocate the raw material costs to the components flowing in the investigated open path flows. If at least one of the products of the overall reaction equation generates a value outside the process boundaries, the cost allocation factor $CA_o^{(c)}$ is calculated using the following convention:

$$CA_o^{(c)} = \frac{PP_o^{(c)}}{\sum_{pd=1}^{PD} PP_o^{(pd)}} \qquad \text{(Eq. 5-3)}$$

in which the superscript *pd* denotes a product and *PD* the total number of products of the overall reaction equation. In case a product *pd* generates multiple specific values, $PP_o^{(pd)}$ represents the maximum specific value obtained.

If no product generates a value outside the process boundaries the allocation is based on the molecular weights of the products:

$$CA_o^{(c)} = \frac{M_o^{(c)}}{\sum_{pd=1}^{PD} M_o^{(pd)}} \qquad \text{(Eq. 5-4)}$$

This case occurs if an overall reaction equation only yields by-products with no value outside the process boundaries (e.g. one or more raw materials react to two or more by-products of no value).

5.1.2 Energy and waste cost (*EWC*)

The *EWC*-indicator quantitatively allocates overall process costs related to utility consumption and waste treatment to a component path flow. The allocation deliberately neglects molecular interactions (e.g. heats of mixing) in mixed process streams and therefore idealizes the distribution of utility and waste treatment costs. The results indicate cost reduction potentials in each specific component path flow. Nevertheless, often only fractions of these potentials can be tapped by retrofit design depending on process constraints (e.g. safety, product quality, environmental regulations, thermodynamic constraints, equipment constraints).

A unit-operation consists of one or more basic sub-operations (e.g. condenser: condensing + cooling). Before allocation it becomes necessary first to attribute a fraction of the energy consumption of each unit-operation to all of its sub-operations. If the exact contributions cannot be easily determined a good estimate is sufficient for screening purposes. Moreover, each component path flow traversing a unit-operation is assigned to one or more of its sub-operations. This assignment depends on the influence a given component path flow has on each sub-operation encountered along its path. If an investigated component path flow has no influence on a given sub-operation along its path the energy consumption of this sub-operation is not considered in the cost allocation. In the opposite case the sub-operation needs to be considered. If there is only a weak influence the decision if the sub-operation is to be considered or not is up to the user. The allocation of process utility costs to a component path flow k ($EC_k^{(c)}$)is then handled in the following manner:

$$EC_k^{(c)} = \sum_{u=1}^{U} PE_u Q_u \frac{m_k^{(c)} A_{u,k}^{(c)}(T_m, p_m)}{\sum_{uk=1}^{UK} m_{u,uk} A_{u,uk}(T_m, p_m)} \qquad \text{(Eq. 5-5)}$$

Here u is the sub-operation index for all sub-operations considered for cost allocation along a component path flow k, U represents the total number of sub-operations considered for that path flow k, uk is the index of all component path flows involved in a given sub-operation u, UK represents the total number of component path flows involved in that sub-operation, and Q_u as well as PE_u represent the specific energy consumption and price of the utility needed for sub-operation u. Sub-operation-specific allocation factors A_u at mean temperatures T_m and pressures p_m (e.g. heating and cooling in a single phase: heat capacity of component) are also used in *(Eq. 5-5)*.

Waste treatment costs only concern open component path flows leaving the process boundaries to a waste treatment facility. Allocation of waste treatment costs $WC_k^{(c)}$ to these path flows is performed in a different manner. Most often waste treatment costs are already pre-allocated because the prices for waste treatment usually depend on the waste composition (e.g. TOC content (Total Organic Carbon), total volume or mass, salt concentration, heavy metal concentration). Therefore, waste treatment costs for components are defined according to mass, volume, and concentration (e.g. ethanol belongs to the TOC category and is allocated according to its mass flow-rate). Unfortunately, the waste cost allocation varies from site to site and company to company. Therefore, the waste cost allocation for component path flow *k* ($WC_k^{(c)}$) can be only generalized by the following equation:

$$WC_k^{(c)} = m_k^{(c)} \cdot \begin{cases} (\rho_{k,\,out})^{-1} WAV_k^{(c)} & \text{(volume allocation)} \\ WAM_k^{(c)} & \text{(mass allocation)} \\ (V_{k,\,out})^{-1} WAC_k^{(c)} & \text{(allocation by conc.)} \end{cases} \qquad \text{(Eq. 5-6)}$$

in which $\rho_{k,\,out}$ and $V_{k,\,out}$ represent the density and volumetric flow-rate of the process stream where open component path flow *k* leaves the process boundaries, $WAV_k^{(c)}$ represents the volume-specific allocation factor for component *c*, $WAM_k^{(c)}$ the mass-specific allocation factor for component *c*, and $WAC_k^{(c)}$ the concentration-specific allocation factor for component *c*. The final *EWC*-indicator covers both energy and waste costs:

$$EWC_k^{(c)} = EC_k^{(c)} + WC_k^{(c)} \qquad \text{(Eq. 5-7)}$$

5.1.3 Reaction quality (*RQ*)

The *RQ*-indicator qualitatively measures the effect of a component path flow *k* upon reactions that occur along its path. Positive *RQ*-values indicate a positive effect on overall plant productivity (defined as the total mole flow-rate of the reactants required per total mole flow-rate of the desired products produced) whereas negative values identify undesirably located component path flows in the process and thus highlight potential for cost savings through mass flow reduction or rerouting of a path flow. The *RQ*-value of a path flow is calculated as the sum of its effects on reactive unit-operations along the path:

$$RQ_k^{(c)} = \sum_{r=1}^{R} \sum_{rk=1}^{RK} \frac{\xi_{r,\,rk,\,k} E_{r,\,rk,\,k}^{(c)}}{\sum_{fp=1}^{FP} n^{(fp)}} \qquad \text{(Eq. 5-8)}$$

$\xi_{r,\,rk,\,k}$ representing the extent of reaction *rk*, $n^{(fp)}$ the mole flow-rate of a desired final product *fp* ({1,…, *FP*}) of the process, *r* the index of reactive unit-operations ({1,…, *R*}) along path flow *k*, and *rk* the index of all reactions {1,…, *RK*} in reactive unit-operation *r* affected by path flow *k*. The definition of the *RQ*-indicator in *(Eq. 5-8)* contains a parameter $E_{r,\,rk,\,k}^{(c)}$ that characterizes the effect of the component flowing in path flow *k* on each reaction involved in the path flow:

$$E_{r,\,rk,\,k}^{(c)} = \begin{cases} +1, \text{ if component } c \text{ in } k \text{ affects reaction } rk \\ \quad \text{so that the total productivity of the} \\ \quad \text{desired products } n^{(fp)} \text{ is increased.} \\ 0, \text{ if component } c \text{ in } k \text{ has no effect on} \\ \quad \text{reaction } rk \text{ and the total productivity of} \\ \quad \text{the desired products } n^{(fp)} \text{ is unchanged.} \\ -1, \text{ if component } c \text{ in } k \text{ affects reaction } rk \\ \quad \text{so that the total productivity of the} \\ \quad \text{desired products } n^{(fp)} \text{ is decreased.} \end{cases} \qquad \text{(Eq. 5-9)}$$

The qualitative values of the effect-parameters $E^{(c)}_{r,\, rk,\, k}$ can be determined depending on the most relevant type of information available: kinetic information, plant experience, or thermodynamic data.

5.1.4 Accumulation factor (AF)

The *AF*-indicator rates the accumulative behaviour in recycle flows and therefore only applies to component cycle path flows. A large accumulation factor often indicates unfavourable build-up in a cycle and can be caused by non-optimal separation or too low reaction conversion. As typical cycle accumulation should be as low as technically feasible for obvious economic reasons, high *AF*-values can thus pinpoint on potentials for cost reduction. High *AF*-values might be desired for valuable raw materials, solvents or auxiliaries.

The *AF*-indicator is calculated as the ratio of a component cycle path flow-rate $m^{(c)}_{z}$ and the sum of all flows of that component leaving the cycle flow ($f^{(c)}_{i,\, a}$ and $d^{(c)}_{i,\, op}$) from any of its vertices *i* of the set of vertices *CP* in the cycle flow:

$$AF^{(c)}_{z} = \frac{m^{(c)}_{z}}{\sum_{i=1}^{I}\left(\sum_{a=1}^{M} f^{(c)}_{i,\, a} + \sum_{op=1}^{OP} d^{(c)}_{i,\, op}\right)} \qquad \text{(Eq. 5-10)}$$

$$\forall i \in CP$$

5.1.5 Total-value added (*TVA*)

The *TVA*-value finally describes the economic impact of a given component path flow on the variable process costs (energy, waste and material cost). It is calculated in the following manner:

$$TVA^{(c)}_{k} = MVA^{(c)}_{k} - EWC^{(c)}_{k} \qquad \text{(Eq. 5-11)}$$

Usually only the negative *TVA*-values designate process improvement potentials in the process. However, a path flow with an important positive *EWC*-value compensated by an even higher *MVA*-value yields a postive *TVA*-value but can still entail an energy cost reduction potential.

5.2 Path flow assessment example: Benzene in the HDA process

In this section the path flow assessment procedure is demonstrated on selected benzene path flows that have already been determined in the example of the previous chapter. The index-values of *k* refer to the benzene path flow number in Table 4-2. The path flow assessment procedure is applied to both, the HDA case study and the Fine Chemical case study but overall results are only later introduced in Chapter 6.

5.2.1 *MVA*-values for benzene path flows *k*=3 and *k*=5

It is assumed that purge stream $d_{PU,\,op}$ is incinerated and fuel credit for 70% of the combustion enthalpy is given. The gross reaction equation for the formation of benzene from raw materials toluene and hydrogen corresponds to the main reaction. The results are shown in Table 5-1.

Table 5-1: Economic values used for the *MVA*-calculation for *k*=3 and *k*=5 (refers to Table 4-2)

k	$PR_k^{(To)}$ [US$/kg]	$PR_k^{(H_2)}$ [US$/kg]	$PP_k^{(Bz)}$ [US$/kg]	$PP^{(CH_4)}$ [US$/kg]	$MVA_k^{(Bz)}$ [kUS$/a]
3	0.3	2.0	0.44 (sales)	0.21 (fuel)	19600
5	0.3	2.0	0.17 (fuel)	0.21 (fuel)	-72

5.2.2 *EWC*-value for benzene path flow *k*=1

The benzene gas cycle path flow causes utility consumption in fired heater FH, the quench and flash operations in FL and compressor CO (Figure 3-4 and Table 5-2). All other vertices involved in the gas cycle do not consume utilities with respect to benzene (reactor RK operates adiabatically, HX1-HX2 exchanges process heat, .PU does not consume utilities, MI only needs elec-

Table 5-2: Data for the *EC*-calculation for benzene path flow *k*=1 (refers to Table 4-2)

Vertex **Sub.-op.** u	**FH** **heating**	**FL (quench)** **cooling**	**FL (flash)** **cooling**	**FL (flash)** **condensing**	**CO** **compressing**
Utility	Natural Gas	Cooling Water	Cooling Water	Cooling Water	Electricity
Energy duty Q_u, [kW]	8680	561	3480[a]	2010[a]	356
Prices PE_u, [US$/GJ]	8.8[b]	1.0[c]	1.0[c]	1.0[c]	13.1
Allocation factor A_u	Heat capacity (gas phase)	Heat capacity (gas phase)	Heat capacity (gas phase)	Heat of vaporization (only Bz, To, Dp)	Molar volume (gas phase)
Temperature T_m, [°C]	522	163	96	96	48
Pressure p_m, [MPa]	3.8	3.4	3.3	3.3	3.6
Total flow-rates involved [kg/h]:					
• Benzene	868	13500	13500	13500	742
• Toluene	20500	5120	5120	5120	93
• Hydrogen	2450	2120	2120	2120	1820
• Diphenyl	94	487	487	487	0
• Methane	17100	19700	19700	19700	16800
$EC_{u,1}^{(Bz)}$, **[kUS$/a]**	**25.0**	**0.2**	**0.9**	**2.2**	**0.6**

a. The total energy consumption for the flash operation (5490 kW) is attributed to two sub-operations: cooling and condensing.

b. Assumes 80% efficiency in the furnace.

c. Assumes an average temperature rise in the cooling water of 5°C after cooling.

tricity for pumping toluene). The gas cycle does not undergo waste treatment – therefore the *EWC*-value is calculated only by allocation of the energy costs. Based on the calculation data from Table 5-2 the final *EWC*-value is then calculated by adding the allocated *EC*-values for all sub-operations ($EWC_1^{(Bz)} = \sum_u EC_{u,1}^{(Bz)} = 29\ \text{kUS\$/a}$).

5.2.3 *RQ*-values for benzene path flows *k*=1 and *k*=2

RQ-values can be assigned only to the benzene gas and liquid cycle path flows because the remaining open benzene path flows do not affect the only reactive unit-operation (vertex RK in Figure 3-4) in the flowsheet. The recycling of benzene has a negative effect on overall benzene productivity due to the equi-

Table 5-3: ***RQ*-calculation for benzene path flow *k*=1 and *k*=2 (refers to Table 4-2)**

k	$E^{(Bz)}_{R1,\,RK,\,k}$ [-]	$E^{(Bz)}_{R2,\,RK,\,k}$ [-]	$\xi_{R1,\,RK}$ [kmol/h]	$\xi_{R2,\,RK}$ [kmol/h]	$n^{(Prod)}$ [kmol/h]	$RQ^{(Bz)}_k$ [-]
1	0	-1	167	2.6	160	-0.02
2	0	-1	167	2.6	160	-0.02

librium side-reaction to diphenyl. Both path flows yield the same results as the indicator only measures the effect qualitatively.

5.2.4 *AF*-values for benzene path flows *k*=1 and *k*=2

The benzene gas cycle path flow comprises flows $f_{FL,\,DS}$, $d_{RK,\,or}$ and $d_{PU,\,op}$ (see Figure 3-4) that respectively leave vertices FL, RK, and PU of the gas cycle while flows $f_{FL,\,PU}$, $d_{DS,\,op}$, $d_{DB,\,op}$ and $d_{DT,\,op}$ leave vertices of the liquid cycle. The corresponding *AF*-values are calculated as illustrated in Table 5-4.

Table 5-4: ***AF*-calculation for benzene path flow *k*=1 and *k*=2 (refers to Table 4-2)**

k	$m^{(Bz)}_k$, [kg/h]	Sum of output flows, [kg/h]	$AF^{(Bz)}_k$, [-]
1	742	12800	0.06
2	126	13400	0.01

5.2.5 *TVA*-values for benzene path flow *k*=1 and *k*=3

Finally, the *TVA*-values for these benzene path flows are calculated by *(Eq. 5-11)* and the results are displayed in Table 5-5.

Table 5-5: ***TVA*-calculation for benzene path flow *k*=1 and *k*=3 (refers to Table 4-2)**

k	$m^{(Bz)}_k$, [kg/h]	$EWC^{(Bz)}_k$ [kUS$/a]	$MVA^{(Bz)}_k$ [kUS$/a]	$TVA^{(Bz)}_k$ [kUS$/a]
1	742	29	0	-29
3	12500	140	19580	19440

5.3 Discussion and conclusions

The assessment indicators that are introduced in the path flow assessment procedure comprise two economic indicators, the *MVA*- and the *EWC*-indicator which only consider the variable cost structure of the process (e.g. raw material costs, variable energy costs, waste disposal costs). Both economic indicators are further summed in the *TVA*-indicator.

The variable costs of a process cannot be allocated to the component path flows in a unique fashion. The flow decomposition procedure, as mentioned in the previous paragraph, already deliberately neglects physico-chemical interactions between open and cycle component path flows of the same component and between component path flows of different components. Most of the time these interactions are only qualitatively known, which makes an exact allocation of the variable energy and waste disposal costs to each component path flow complex. The allocation procedure of the energy costs for the *EWC*-indicator (see Section 5.1.2) is based on the following assumptions:

a) The energy consumption of a given unit-operation can be allocated to its basic physico-chemical sub-operations (e.g. heating, condensing, compressing).

b) Sub-operations can be assigned to a given component path flow.

c) Characteristic physical parameters for each sub-operation can be used to allocate its energy consumption (e.g. heat capacity for heating or cooling in the same phase, enthalpy of vaporization for vaporization or condensation).

In principle, the allocation of the energy consumption of a unit-operation to its sub-operations (a) can always be calculated if enough physical data is available about the sub-operation and its corresponding input and output flows. When confronted with insufficient data, assumptions have to be made accordingly. Further, the assignment procedure (b) is not entirely explicit as described in Section 5.1.2. Finally, the allocation of the energy consumption of a given sub-operation to all component path flows that are assigned to it (c) heavily depends on the chosen physical parameter. On the other hand, the waste disposal costs of a process are assumed to be pre-allocated (see Section 5.1.2) if the waste disposal facility is not part of the investigated process. Therefore, the waste disposal costs can be explicitely allocated to each component path flow.

The allocation procedure for the material costs is based on two different types of cost allocation factors (see Section 5.1.1). In case the overall reaction equation for a given component path flow yields at least one product that generates a value outside the process boundaries the material costs are allocated according to the values of the products with *(Eq. 5-3)*. If no product generates a value outside the process boundaries the material costs are allocated according to the molecular weights of the products with *(Eq. 5-4)*. It has to be noted though, that allocation procedures always remain subjective in nature as concluded by Frischknecht (1998)**[21]** in the context of eco balances. Likewise, the allocation procedure is unresolved in the case of an intermediate product that is not assigned an economic value outside the process boundaries, yet is required to produce a valuable product in a subsequent process.

6 GENERATION OF RETROFIT OPTIONS

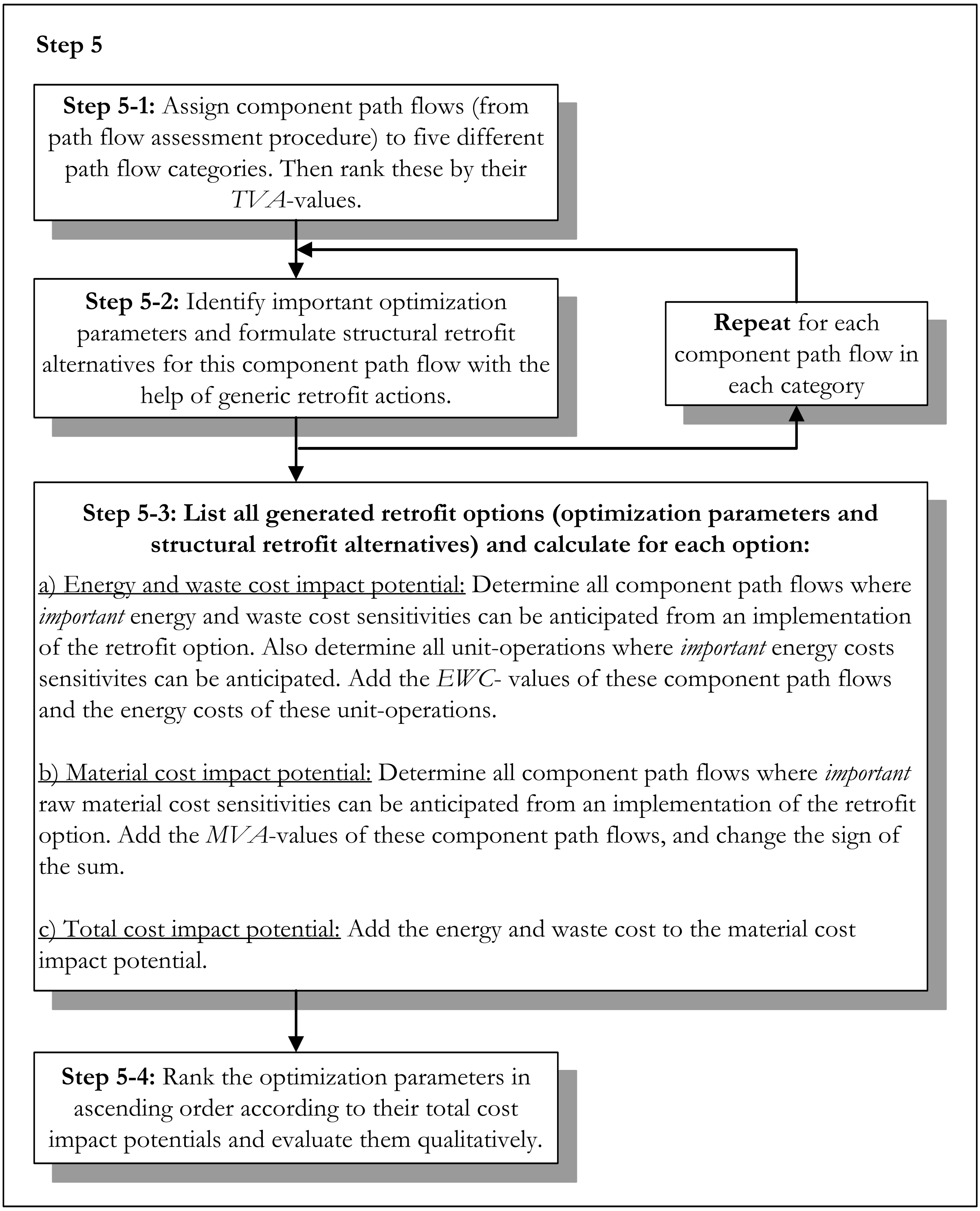
6.1 Overview

In this chapter, the next step (**Step 5** – see Figure 2-3) of the screening method is represented for generating retrofit options (optimization parameters and structural retrofit alternatives) from the results of the flow decomposition and assessment procedure (**Steps 3** and **4**) from the application to a given process. This approach is summarized in Figure 6-1. In **Step 5-1**, the component path flows are assigned to five different path flow categories according to their indicator values (from the path flow assessment procedure in Section 5) and then ranked in each category by their *TVA*-values. In **Step 5-2**, important process parameters (referred to as *optimization parameters*) as well as structural alternatives to modify the process (referred to as *structural retrofit alternatives*) are identified. They target at economic process improvement potentials as indicated by the economic performance indicators (*MVA*- and *EWC*-indicators). Both parameters and structural alternatives are referred to as *retrofit options* in the following. At this level of the method, general process actions – formulated in an abstract manner (referred to as *generic retrofit actions*) – are introduced and used as a check-list for each component path flow and path flow category (Table 6-1). In **Step 5-3**, new economic indicators are then introduced to rate the *cost impact potentials* of the identified optimization parameters and of the generated structural retrofit alternatives on the variable process costs (explained in more detail in Section 6.2). At last, the optimization parameters and structural retrofit alternatives are ranked in **Step 5-4** and qualitatively evaluated.

6.2 Description of the generation procedure for retrofit options

6.2.1 Assignment to path flow categories (Step 5-1)

Each generated component path flow is attributed to four different path flow categories according to the path flow type (open or cycle) and the *RQ*-indica-



Step 5

Step 5-1: Assign component path flows (from path flow assessment procedure) to five different path flow categories. Then rank these by their *TVA*-values.

Step 5-2: Identify important optimization parameters and formulate structural retrofit alternatives for this component path flow with the help of generic retrofit actions.

Repeat for each component path flow in each category

Step 5-3: List all generated retrofit options (optimization parameters and structural retrofit alternatives) and calculate for each option:

a) Energy and waste cost impact potential: Determine all component path flows where *important* energy and waste cost sensitivities can be anticipated from an implementation of the retrofit option. Also determine all unit-operations where *important* energy costs sensitivites can be anticipated. Add the *EWC*- values of these component path flows and the energy costs of these unit-operations.

b) Material cost impact potential: Determine all component path flows where *important* raw material cost sensitivities can be anticipated from an implementation of the retrofit option. Add the *MVA*-values of these component path flows, and change the sign of the sum.

c) Total cost impact potential: Add the energy and waste cost to the material cost impact potential.

Step 5-4: Rank the optimization parameters in ascending order according to their total cost impact potentials and evaluate them qualitatively.

Figure 6-1: Scheme for generating retrofit options from the results of the screening procedure (Step 5 refers to the master scheme in Figure 2-3)

tor value (*RQ*-values ≤ 0 or >0). The third category (cycle path flows, *RQ*-values ≤ 0) is further divided into sub-categories according to the *AF*-indicator values (*AF*-values ≤ 1 or > 1) in order to differentiate between low and high *AF*-values. In each category the assigned component path flows are then sorted in ascending order according to their *TVA*-values, which ensures that the path flows are listed in order of economic impact. Because the number of path flows increases considerably with regard to the complexity of a process (i.e. increasing number of supply and demand flows in a process graph) a cut-off *TVA*-value can be defined for practical reasons in order to remove path flows with low economic impact and thus limit the number of path flows in a later detailed analysis. Yet, this procedure bears the risk that some potential retrofit options are overlooked.

6.2.2 Identification of retrofit options (Step 5-2)

Different generic retrofit actions are proposed for each category in the check-list of Table 6-1. Each path flow remaining after the cut-off is analyzed with the help of these category-specific retrofit actions to determine which action(s) is (are) best suited to increase the economic performance for the investigated path flow. This step mostly aims at pre-screening the component path flows at a low-detail level. The respective retrofit actions are formulated in an abstract fashion and do not comprise any detailed instructions how to actually perform these actions in the context of the investigated process.

As a next step, important optimization parameters and structural retrofit alternatives for the investigated process are then determined on the basis of the selected generic retrofit actions. This step represents the most challenging task in the procedure to generate retrofit alternatives. In fact, at this level of the procedure the user has to perform the following tasks :

a) The most important process parameters that affect the selected generic retrofit actions have to be identified (optimization parameters).

b) Possibly, some generic retrofit actions might not be influenced by any of the optimization parameters identified in (a). Furthermore, some generic retrofit actions might only be carried out partially by a process cost optimization with the optimization parameters from (a). In both cases, structural retrofit alternatives have to be additionally formulated to further improve the economic performance of the investigated component path flows.

As process retrofit design is complex and highly case-specific in its nature an automated procedure is difficult to conceive at this step. Therefore, the author proposes to use and combine specific process and general engineering knowledge. However, the user need not yet specify the structural retrofit alternatives in detail at this stage. The detailed formulation of the alternatives can take place in a later step when attainable cost savings potentials are calculated in detail by using rigorous simulation. Frequently, several optimization parameters or structural retrofit alternatives generated by this approach tap the economic improvement potential residing in multiple path flows. In some cases the optimization parameters or structural alternatives can also aim at reducing the energy cost requirement(s) for a single (multiple) unit-operation(s).

6.2.3 Total cost impact potential of retrofit options (Step 5-3)

Next, all optimization parameters and structural retrofit alternatives that have been previously identified in **Step 5-2** are listed and the cost impact potentials on material and energy costs calculated. Using general knowledge of the behaviour of process-systems a process engineer can qualitatively judge the effect that a change of an operating parameter or the implementation of a structural retrofit alternative might have on component path flows or unit-operations of the process. The process engineer is not required to judge the *direction* of the effect (e.g. if temperature is increased in a reactor, is the path flow-rate of a product from that reactor going to increase or decrease?). A simple evaluation is only necessary: Is the effect on a given component path flow or unit-operation expected to be *important* or *negligible*? This qualitative evaluation procedure is then used to determine which component path flow(s) and unit-operation(s) are expected to exhibit an *important* cost sensitivity to a manipulation of a given optimization parameter. The same qualitative evaluation is also carried out if a structural retrofit alternative is implemented. The costs in both evaluations refer to the *MVA*-value and *EWC*-value in case of component path flows (as calculated in the path flow assessment procedure) and to energy costs in case of unit-operations (as given by the energy balance of the base case). This qualitative evaluation is repeated for all retrofit options. It should be noted that this procedure is, of course, highly subject to the user's individual judgement, yet also contributes to a better understanding of the cause-effect relationships in the process. Once the qualitative evaluation has been carried out for all retrofit options, the cost impact potentials are calculated *for each retrofit option* as follows:

a) **Energy and waste cost impact potential:** First, the component path flows that have been judged to exhibit an *important* cost sensitivity with respect to their allocated energy and waste costs are grouped together. Then, the unit-operations that have been judged to show an *important* sensitivity with respect to their energy costs are added to the latter group. The energy and waste cost impact potential for the investigated retrofit option is then calculated by adding the *EWC*-values of these component path flows and the energy costs of these unit-operations based on the path flow assessment results.

b) **Material cost impact potential:** The material cost impact potential for each retrofit option is calculated in analogy to the energy and waste cost impact potential. The component path flows that have been judged to exhibit an *important* cost sensitivity with respect to their *MVA*-values are grouped together. In order to calculate the material cost impact potential for a given optimization parameter the *MVA*-values of these component path flows have to be added. Since this value is referred to as "material cost impact potential", while it generally exhibits a negative value, the algebraic sign of the calculated sum is switched accordingly.

c) **Total cost impact potential:** The total cost impact potential is finally calculated as the sum of the energy and waste cost impact potential and the material cost impact potential for each optimization parameter. This sum is not necessarily equivalent to the sum of *TVA*-values of the component path flows identified for the energy and waste cost and material cost impact potential because some component path flows might only be sensitive to a change in either cost category. Moreover, energy costs of unit-operation(s) might also be included in the sum.

The total cost impact potential, calculated for optimization parameters, is not meant as a cost reduction target, but merely indicates the impact magnitude of the designated parameter on the energy and material costs of the investigated process. More precisely it indicates the cumulated "leverage effect" or cost effect of each generated optimization parameter on the variable process cost based on the component path flow assessment results. The total cost impact potential is then used to rank the generated optimization parameters relatively to each other. The later application of this evaluation to both case studies will contribute to a better understanding of the rough evaluation procedure.

The total cost impact potential, calculated for structural retrofit alternatives, equally serves as a rough economic performance indicator to estimate the order of magnitude of the variable cost savings to be expected from the investigated structural retrofit alternative. The interpretation of the meaning of the impact potential for a structural retrofit alternative is different as compared to optimization parameters. This is due to the fact that in case of structural retrofit alternatives the direction of the effects on component path flows and unit-operations can be predicted more easily since these are actually intended to "break" trade-offs in the process. The total cost impact potential can thus be used to rank the different structural retrofit alternatives among each other.

6.2.4 Ranking and qualitative evaluation of retrofit options (Step 5-4)

Finally, the optimization parameters and the structural retrofit alternatives are ranked in ascending order according to their total cost impact potentials. The optimization parameters are then discussed qualitatively on their expected effect in a parameter optimization. The structural retrofit alternatives are also qualitatively evaluated on the attainable cost savings to be expected.

6.3 Generic retrofit actions

Depending on the path flow categories previously mentioned different generic retrofit actions targeting at economic improvement potentials are shown in Table 6-1. The list is viewed only as an initial proposition for generic actions and does not claim to be complete. The application of this methodology to new case studies would certainly yield additional generic retrofit actions. Typical retrofit actions include:

Table 6-1: Generic retrofit actions for different path flow categories

Component path flows	Generic retrofit action[a]
All categories	• Reduce the specific energy consumption of the path flow
Category 1: Open component path flows, $RQ \leq 0$	• Remove/reduce the open path flow-rate at the source • Reroute (partially) the open path flow in the process • If $RQ = 0$, recycle the open path flow only when this recycling yields a positive effect on productivity • Replace the open path flow component with a better component • Increase the specific value $PP_o^{(c)}$ of the open path flow
Category 2: Open component path flows, $RQ > 0$	• Optimize/reduce the open path flow-rate • Recycle (partially) the open path flow to the process • Increase the specific value $PP_o^{(c)}$ of the open path flow
Category 3a: Cycle component path flows, $RQ \leq 0$, $AF > 1$	• Remove/reduce the cycle path flow at the source • Change from a cycle to an open path flow • Reduce the accumulation factor of the cycle path flow • Replace the cycle path flow component with a better component • Reroute (partially) the cycle path flow in the process
Category 3b: Cycle component path flows, $RQ \leq 0$, $AF \leq 1$	• Remove/reduce the cycle path flow at the source • Change from a cycle to an open path flow • Replace the cycle path flow component with a better component • Reroute (partially) the cycle path flow in the process
Category 4: Cycle component path flows, $RQ > 0$	• Optimize the cycle path flow-rate • Reroute (partially) the cycle path flow in the process

[a] See text for detailed explanations.

- **Reducing the specific energy consumption of a component path flow:** This generic retrofit action can be used in all path flow categories of Table 6-1. If few or no changes to a path flow and its flow-rate can be made, there might still be a chance of reducing its specific *EWC*-value (ratio of *EWC*-value and flow-rate of a given path flow). Such a situation could occur, if one or more unit-operations along the path flow still exhibit optimization potentials with regard to utility consumption (e.g. parametric optimization of the unit, structural modification of the unit, or replacement of the unit with a less energy consuming unit-operation). As an example, column internals with higher separation efficiency can reduce the utility requirements of a separation column (distillation, absorption) without necessarily impacting on the separation task and thus the path flows involved in the separation.
- **Remove/reduce a component path flow at the source:** If both cycle and open path flow-rates exhibit *RQ*-values below or equal to zero there is an incentive to reduce their flow-rates or totally remove them when possible. This can be achieved by reducing/removing them where they are introduced to the process or reduce or eliminate the reaction that generates them in the process.
- **Reroute (partially) a component path flow in the process:** This generic retrofit action considers a partial or complete rerouting of the investigated path flow either onto a new path flow or onto an existing path flow of the component involved. If the specific *EWC*-value of another path flow of the same component is lower than that of the investigated path flow, rerouting to that path flow could be an interesting retrofit alternative. However, if rerouting can be performed only by altering the appropriate process operating parameters, trade-offs have to be expected. Also, the *RQ*-value has to be taken into consideration when rerouting to an existing path flow is studied. Only rerouting to a path flow with an equal or higher *RQ*-value is recommended. Equally, if rerouting of a path flow to a new path flow is considered the *RQ*-value of

the new path flow should be equal to or higher than the value of the investigated one as productivity might otherwise decrease.

- **Recycle an open component path flow to the process:** Open path flows that have an *RQ*-value equal to or greater than zero have a positive impact on productivity and should only be recycled if this generates either a positive impact on productivity or has a reasonable impact on the process material costs. This generic retrofit action is especially suited for path flows with *RQ*-values greater than zero.
- **Replace a path flow component with a better component:** Another generic retrofit action consists in replacing the component in the investigated path flow with an alternate component (e.g. different solvent with the same or better service quality). The candidate component should lead to lower *EWC*-values, higher *RQ*-values, or lower *AF*-values in the investigated component path flow. The new separation pattern should moreover lead to lower *EWC*-values on all component path flows that are affected by the component substitution.
- **Increase the specific path flow value $PP_0^{(c)}$ of an open component path flow:** A specific path flow value can be influenced only outside the process boundaries. This can be achieved by either different use of the component path flow outside the process (e.g. selling a valuable component instead of incinerating it), or by economic means (e.g. increase of market value). However, the latter strategy is entirely part of the overall business strategy and is mostly governed by market laws.
- **Optimize/reduce a cycle component path flow-rate or optimize an open component path flow-rate:** Open and cycle path flows that yield positive *RQ*-values have a positive effect on productivity. If these exhibit large *EWC*-values, there may still be potential in flow-rate optimization. In this case, retrofitting can be typically carried out by manipulating appropriate process operating parameters. As usually reactants are recycled in a process – when the conversion of the desired reaction is not

complete – the resulting reactant cycle path flows exhibit positive *RQ*-values. Therefore, reducing these reactant cycle path flow-rates by increasing the conversion can be viewed as another generic retrofit action.

- **Reduce the accumulation factor of a cycle component path flow:** A high accumulation factor in a cycle component path flow with a *RQ*-value lower than zero indicates an unfavorable build-up of that component in a recycle. This kind of situation can occur if unwanted side-products or components with inert behaviour are too sharpely separated and recycled in the process. Often this is indirectly caused by too high recoveries or purities of valuable products in a separation. In order to lower the accumulation factor, a purge could be introduced, a separation manipulated or the reaction conditions improved.

6.4 HDA case study

6.4.1 Flow decomposition and component path flow assessment results

Table 6-2 shows the results of the flow decomposition and assessment procedure applied to the HDA case study. The path flows are sorted according to ascending *TVA*-values in each path flow category. Path flows with highest cost impact potentials appear at the top of each category's list.

In this case study it is assumed that open path flows O1-O7, O9, O12, O13, and O14 are incinerated and fuel-credit (production of steam) is given for 70% of each component's heat of combustion. In the first category of Table 6-2, methane, benzene and diphenyl open path flows O1-O5 display negative *TVA*-values. No raw-material purchase costs are allocated to methane open path flows O6 and O7 because these are supplied to the process as an impurity in the fresh hydrogen feed. The other methane open path flows O1 and O2 are generated in reactor RK (Figure 3-4) as a by-product of the main reaction *(REq. 3-1)* and account for raw material costs according to *(Eq. 5-2)*. Since methane is a by-product of the main reaction in reactor RK but also generates

Table 6-2: Component path flow assessment results and ranking: HDA case study

Nr.	Co.	Path[a]	Mass Flow [kg/h]	RQ [-]	AF [-]	EWC [kUS$/a]	MVA [kUS$/a]	TVA[b] [kUS$/a]
Category 1: Open path flows, $RQ \leq 0$								
O1	CH_4	$s_{RK,\,ir} - d_{PU,\,op}$	2560	0	-	7	-11833	-11740
O2	CH_4	$s_{RK,\,ir} - d_{DS,\,op}$	120	0	-	1	-553	-554
O3	Bz	$s_{RK,\,ir} - d_{PU,\,op}$	124	0	-	1	-71	-72
O4	Dp	$s_{RK,\,ir} - d_{DT,\,op}$	393	0	-	2	-25	-27
O5	Bz	$s_{RK,\,ir} - d_{DS,\,op}$	9	0	-	4	-5	-9
O6	CH_4	$s_{MI,\,ip} - d_{DS,\,op}$	12	0	-	1	20	19
O7	CH_4	$s_{MI,\,ip} - d_{PU,\,op}$	255	0	-	15	419	404
O8	Bz	$s_{RK,\,ir} - d_{DB,\,op}$	12500	0	-	140	19580	19440
Category 2: Open path flows, $RQ > 0$								
O9	H_2	$s_{MI,\,ip} - d_{PU,\,op}$	304	1.06	-	70	-3660	-3730[c]
O10	To	$s_{MI,\,ip} - d_{RK,\,or}$	15400	1.04	-	554	0	-554
O11	H_2	$s_{MI,\,ip} - d_{RK,\,or}$	331	1.06	-	67	0	-67
O12	H_2	$s_{MI,\,ip} - d_{DS,\,op}$	3	1.06	-	0	-33	-33
O13	To	$s_{MI,\,ip} - d_{PU,\,op}$	16	1.04	-	0	-16	-16
O14	To	$s_{MI,\,ip} - d_{DB,\,op}$	4	1.04	-	1	0	-1
Category 3: Cycle path flows, $RQ \leq 0$								
a) $AF > 1$								
C1	CH_4	Gas cycle	16800	0	5.7e+0	1030	0	-1030
b) $AF \leq 1$								
C2	Bz	Gas cycle	742	-0.02	5.8e-2	29	0	-29
C3	Bz	Liquid cycle	126	-0.02	9.4e-3	6	0	-6
Category 4: Cycle path flows, $RQ > 0$								
C4	H_2	Gas cycle	1820	1.06	5.9e+0	459	0	-459
C5	To	Liquid cycle	5010	1.04	4.4e+1	233	0	-233
C6	Dp	Liquid cycle	94	0.02	2.4e-1	4	0	-4
C7	To	Gas cycle	93	1.04	1.8e-2	4	0	-4

a. The abbreviations refer to the vertices of the process graph in Figure 3-4.

b. The sum of the TVA-values of all component path flows in all categories yields a type of marginal income as known in business administration (sales - variable process costs) – the marginal income of the HDA process amounts to 1295 kUS$/a.

c. The incineration of hydrogen yields 1200 kUS$/a – without incineration the *TVA*-value would thus amount to 4930 kUS$/a.

a value outside the system boundaries (fuel credit) the raw material costs are allocated to benzene as well as methane according to *(Eq. 5-3)*. Therefore open path flows O1 and O2 score negative *TVA*-values, as the obtained fuel credit does not compensate the allocated raw material costs. Open path flow O8 contains the desired product benzene, and thus exhibits the highest *TVA*-value of the process. All open path flows of the first category show *RQ*-values of zero. The high *EWC*-value of benzene open path flow O8 is mainly related to its high flow-rate.

In contrast to the results in the first category all *TVA*-values for open path flows in the second category are negative. Hydrogen open path flow O9 scores a high negative *TVA*-value in the process, almost exclusively because the incineration yields much less value than the original purchase cost. The explanation for the high negative *TVA*-value for toluene open path flow O10 is analogous to the previous discussion on path flow O8. The *RQ*-values in the second category are uniformly above one (only reactant path flows exist in this category).

Methane and hydrogen cycle path flows C1 and C4 – both in the gas cycle – score the highest negative *TVA*-values in the third and fourth category of Table 6-2, respectively. As discussed before, cycle path flows cannot be assessed by the *MVA*-indicator and are therefore uniformly set to *MVA*-values of zero. The *TVA*-values then only depend on the generated *EWC*-values. Both cycle path flows C1 and C4 also have similar high *AF*-values, only exceeded by toluene cycle path flow C5. In the third category benzene cycle path flows C2 and C3 show undesirable, slightly negative *RQ*-values while methane cycle path flow C1 essentially acts as an inert in reactor RK ($RQ = 0$). In the fourth category cycle path flows C4, C5, and C7 have *RQ*-values above one, only diphenyl cycle path flow C6 shows a low positive *RQ*-value of 0.02.

6.4.2 Identification of optimization parameters and structural retrofit alternatives

Starting from the assessment results for the HDA process this section discusses in order of ascending *TVA*-values which generic retrofit actions are found to be applicable to the corresponding component path flows. In this case no cut-off *TVA*-value is chosen for examplary purposes. After identifying the applicable generic retrofit actions the most important optimization parameters and/or possible structural retrofit alternatives resulting from these are discussed (see Table 6-3). The abbreviations for vertices and edge flows of the HDA process in the discussion refer to the nomenclature used in the process graph of Figure 3-4.

Especially methane open path flow O1 and also O2 display high negative *TVA*-values since these two path flows are generated by the main reaction in reactor RK. These high values follow from the raw material costs that are allocated according to *(Eq. 5-3)* to both path flows. As methane is a coupled by-product of the production the *MVA*-values, which mainly contribute to the high negative *TVA*-values, cannot be influenced without changing the reaction chemistry of the HDA process. In this thesis retrofitting a process by altering its reaction chemistry is not taken considered. It is argued that if the reaction chemistry can be altered usually a large part of the process plant would need to be modified. Often such changes lead to building completely new plants when retrofitting the existing plant is not economically profitable. For this reason this kind of retrofit strategy is deliberately not considered by the author. The methane open path flows O1 and O2 are therefore not taken into account in the process of generating retrofit alternatives.

Hydrogen open path flow O9 displays a high negative *TVA*-value in the investigated HDA process because the high hydrogen purchase cost largely exceeds the fuel credit returned by incineration in $d_{PU,\,op}$ (Figure 3-4). Because hydrogen open path flow O9 is assigned to the second category of Table 6-1 (*RQ* = 1.12), path flow recycling, output value increase, and flow-rate optimization or reduction are suggested as possible generic retrofit actions. Assuming that the purge stream has to be incinerated and that the fuel credit cannot be increased, recycling and flow-rate optimization of hydrogen path flow O9 are applicable generic retrofit actions. In order to recycle hydrogen open path flows O9 as well as O12 (same situation) a hydrogen/methane separation method (Table 6-3) is required, as otherwise both components in the purge stream cannot be handled independently from each other. Further, this structural retrofit alternative also signifies a possible way to reduce the accumulation factor of the methane cycle path flow C1 (Category 3a in Table 6-2) by increased purging without reducing the flow-rate of hydrogen cycle path flow C4. Again, the hydrogen/methane separation follows as a possibility to optimize the hydrogen path flow-rate in C4 (fourth category in Table 6-2) independently from methane cycle path flow C1.

The above mentioned generic retrofit actions can also be performed by varying the appropriate process operating parameters with the exception of hydrogen open path flows O9 and O12 that cannot be recycled to the reactor RK by varying operating parameters. The high accumulation factor of the methane cycle path flow C1 can be reduced by increasing the purge in PU (Figure 3-4). The same operating parameter can be varied to optimize the flow-rate of hydrogen path flow C4. In both cases the hydrogen feed flow-rate to the process ($d_{MI,\,ip}$ in Figure 3-4) has to be adjusted accordingly.

The toluene cycle path flow C5 – listed in the fourth category of Table 6-2 – also shows a high *EWC*-value and a high negative *TVA*-value, accordingly. Since toluene is one of the raw materials of the process a high accumulation factor is desired in order to recycle it as much as possible. However, optimizing its flow-rate might still be a possible generic retrofit action especially as toluene is the limiting reactant in the main reaction *(REq. 3-1)* of reactor RK (Figure 3-4). Therefore, optimizing the toluene cycle path flow-rate in C5 will also affect the conversion in reactor RK. This can be done by varying the toluene recovery in the bottom product of distillation column DT (reflux ratio) while holding the diphenyl recovery in the distillate constant. At the same time the toluene feed-rate to the process in $d_{MI,\,ip}$ needs to be adjusted to keep the benzene production-rate constant as highlighted in Table 6-3. No structural retrofit alternatives are proposed for this generic retrofit action.

Table 6-3: Applicable generic retrofit actions and resulting optimization parameters as well as structural retrofit alternatives: HDA case study

Generic retrofit action [path flow(s)][a]	Optimization parameters[b] [label][c]	Structural retrofit alternatives[b] [label][d]
• Hydrogen recycling to the reactor [O9, O12]	-	• Introduce a hydrogen/ methane separation method [HS1]
• Reduction of the accumulation factor of the methane cycle path flow [C1]	• Vary the purge in PU while adjusting the hydrogen feed-rate to keep the benzene production rate constant [HP1]	• Introduce a hydrogen/ methane separation method [HS1]
• Optimization of the hydrogen path flow-rate [C4]	• Vary the purge in PU while adjusting the hydrogen feed-rate to keep the benzene production rate constant [HP1]	• Introduce a hydrogen/ methane separation method [HS1]
• Optimization of the toluene path flow-rate [C5]	• Vary the reflux ratio in column DT to vary the toluene recovery in the bottom product and the conversion in reactor RK while the diphenyl recovery in the distillate is kept constant – adjust the toluene feed-rate to the process accordingly [HP2]	-
• Better vapor/liquid-separation at vertex FL [O3]	• Vary the coolant flow-rate in the flash-unit in vertex FL [HP4]	• Increase the heat-transfer area in vertex FL [HS2] • Use a different utility for vertex FL [HS2]
• Diphenyl recycling to the reactor [O4]	• Vary the reflux ratio in column DT to vary the diphenyl recovery in the distillate while the toluene recovery in the bottom product is kept constant [HP6]	• Bypass column DT [HS3]
• Reduction of the diphenyl open path flow at the source [O4]	• Vary the reactor RK pressure [HP5] • Vary the reactor RK feed temperature [HP3]	• Introduce a more selective catalyst for reactor RK [HS4]

a. Generic retrofit actions (Table 6-1) are applied to the component path flow(s) from Table 6-2 in brackets.

b. The abbreviations refer to the vertices of the process graph in Figure 3-4.

c. The labels shown in brackets refer to the optimization parameters of Table 6-4.

d. The labels shown in brackets refer to the structural retrofit alternatives of Table 6-5.

Benzene open path flow O3 is due to a non-sharp separation in the flash unit in vertex FL (Figure 3-4). The path flow displays a negative *TVA*-value in the first category of Table 6-2. The application of the flow-rate reduction action in this category leads to improving the gas-liquid separation efficiency in vertex FL so that the raw material losses induced by purging valuable benzene can be reduced. The benzene flow-rate could be reduced by increasing the coolant flow-rate (optimization parameter) to both the flash unit and the water quench cooler and thus lowering the flash outlet temperature to increase the separation efficiency. As structural retrofit alternatives an increase of the heat-exchange surface in vertex FL (flash unit and water quench cooler) or a lower temperature cooling utility are proposed.

Another savings potential is indicated by the negative *TVA*-value of diphenyl open path flow O4 in the first category of Table 6-2. Since the side-reaction leading to the formation of diphenyl is reversible, recycling diphenyl open path flow O4 represents an applicable generic retrofit action. Either distillation column DT could be completely bypassed as a structural retrofit alternative, or the diphenyl recovery in the distillate of column DT could be increased by the parameter variation described in Table 6-3. Alternatively, the generic retrofit action that aims at reducing the diphenyl flow-rate in O4 is proposed. This can be performed by either improving the selectivity of the catalyst (structural retrofit alternative) or by varying the pressure or the feed temperature of reactor RK (optimization parameters).

The rest of the path flows only show little room for improvement potential and are therefore not considered for identifying optimization parameters or structural retrofit alternatives.

6.4.3 Discussion of the identified optimization parameters

The energy and waste cost impact potentials, material cost impact potentials and total cost impact potentials are calculated for the identified optimization parameters and displayed in Table 6-4. This is done by first determining important energy and waste cost sensitive component path flows and important energy cost sensitive unit-operations resulting from each variation of an optimization parameter. The *EWC*-values of these component path flows and the energy costs of these unit-operations are then added for each optimization parameter (see detailed explanations in Section 6.2.3). The results are sorted according to the total cost impact potentials in descending order and subsequently discussed.

The variation of the purge (parameter HP1) influences the methane and hydrogen open path flow-rates C4 and C1 and at the same time requires adjusting of the hydrogen feed-rate ($d_{MI,\ ip}$) to the process in order to keep the production rate of benzene constant. Therefore, parameter HP1 has an impact on cycle path flow-rates C1, C4, and hydrogen open path flow-rate O9 and thus displays by far the highest total cost impact potential among the optimization parameters. However this parameter is constrained by the fact that the hydrogen/toluene-ratio may not be decreased below a ratio of 5 (increased coking occurs on the solid-bed catalyst in reactor RK as pointed out by Douglas (1988)**[13]**).

The variation of the toluene recovery in the bottom product of distillation column DT as described in Table 6-4 (parameter HP2) impacts on toluene cycle path flow-rate C5 as well as on the cooling duty of column DT (not on the heating duty because of heat integration – see Figure 3-4). Since toluene is the limiting reactant in the main reaction *(REq. 3-1)* of reactor RK, the variation also impacts on the conversion of this reaction. Therefore, also the hydrogen cycle path flow C4 and the hydrogen open path flow O9 are impacted as well. If the toluene recovery is varied the fresh toluene feed-rate to the process has to be adjusted in turn to keep the benzene production rate constant. The variation scores second priority in Table 6-4.

Parameters HP3, HP5, and HP6 primarily aim at reducing diphenyl open path flow O4. An increase of the diphenyl recovery in the distillate of column DT (parameter HP6), as explained in Table 6-4, however leads to a higher diphenyl cycle path flow-rate in C6. The total cost impact potential is therefore based on the diphenyl open path flow O4, the diphenyl cycle path flow C6, and the cooling duty needed in the condenser of column DT. Parameters HP3 and HP5 on the other hand aim at reducing the diphenyl formation in reactor RK without necessarily impacting the diphenyl cycle path flow-rate. Further, parameter HP5 also impacts on the compressor duty in vertex CO and param-

Table 6-4: Total cost impact potentials of the identified optimization parameters: HDA case study

Label	**Optimization parameters from Table 6-3**[a]	**Impact on**[b]	**Energy & waste cost impact potential [kUS\$/a]**	**Material cost impact potential [kUS\$/a]**	**Total cost impact potential [kUS\$/a]**	**Referenced in literature**
HP1	Vary the purge in PU while adjusting the hydrogen feed-rate to the process	C1, C4, O9	1560	3660	5220	Referenced[c]
HP2	Vary the reflux ratio in column DT to vary the toluene recovery in the bottom product and the conversion in reactor RK while the diphenyl recovery to the distillate is kept constant – adjust the toluene feed-rate to the process accordingly	C4, C5, O9, cooling duty in DT	790	3660	4450	Referenced[c]
HP3	Vary the reactor RK feed temperature (vary furnace FH duty)	O4, furnace duty of FH	2190	25	2215	Referenced[c]
HP4	Vary the coolant flow-rate in the flash-unit of vertex FL	O2[d], O3, O5, O6[d], O13, cooling duty of FL	174	92	266	Referenced[c]
HP5	Vary the reactor RK pressure (vary pressure in compressor CO)	O4, compressor duty of CO	136	25	161	

Table 6-4: Total cost impact potentials of the identified optimization parameters: HDA case study

Label	Optimization parameters from Table 6-3[a]	Impact on[b]	Energy & waste cost impact potential [kUS$/a]	Material cost impact potential [kUS$/a]	Total cost impact potential [kUS$/a]	Referenced in literature
HP6	Vary the reflux ratio in column DT to vary the diphenyl recovery in the distillate while the toluene recovery in the bottom product is kept constant	O4, C6, cooling duty of DT	35	25	60	Referenced[c]

a. The abbreviations refer to the vertices of the process graph in Figure 3-4.

b. Refers to the important energy and waste cost sensitive component path flows and the important energy cost sensitive unit-operations. The component path flow abbreviations refer to Table 6-2.

c. Fisher et al. (1987)**[18]**

d. Only the *EWC*-value is impacted.

eter HP3 also impacts on the furnace duty in vertex FH. As the furnace consumes a considerable amount of energy (roughly 8.5 MW) parameter HP3 therefore scores the third highest total cost impact potential. However, both feed-temperature and pressure in reactor RK cannot probably be freely manipulated to improve the selectivity without also affecting the conversion of the main reaction *(REq. 3-1)*. Besides, lowering the pressure too much might be constrained by the desired production capacity for the plant. In turn, increasing the pressure might quickly be constrained by equipment pressure limits.

The benzene and toluene open path flows O3, O5 and O13 are mainly affected, if the coolant flow-rate to the quench and flash unit-operation in vertex FL is varied. The *EWC*-values of methane open path flows O2 and O6 are also slightly affected as the condensation duty in stabilising column DS would be reduced. However, these two values are almost negligible. The total cost impact potential for this optimization parameter (parameter HP4) does not only take account of these path flows but also includes the costs for the cooling requirements in that vertex and scores fourth priority in Table 6-4.

A process optimization of the same HDA process flowsheet was performed by Fisher et al. (1987)[18]. Fisher et al. selected the reactor conversion in reactor RK, the purge-split in PU, the furnace-duty in FH, the coolant flow-rate in FL, and the reflux ratio of distillation column DT for a process optimization. A local cost sensitivity analysis was also performed for these parameters and especially the conversion and the purge parameter were found to be an order of magnitude more cost-sensitive than the other parameters. The same optimization parameters were also identified by the proposed approach. The reactor conversion itself is indirectly influenced by other parameters. It is mostly influenced by the reflux ratio of column DT (parameter HP2). It can be concluded from the results of this approach that the conversion and purge parameter are by far the most important parameters for a process optimization as they score the highest total cost impact potentials in Table 6-4.

6.4.4 Discussion of the generated structural retrofit alternatives

The energy and waste cost, material cost and total cost impact potentials are calculated for the generated structural retrofit alternatives and displayed in Table 6-5. This is done by determining the component path flows where important energy and waste cost savings can be anticipated and by determining unit-operations where important energy cost savings can be expected from each structural retrofit alternative. The *EWC*-values of these component path flows and the energy costs of these unit-operations are then added for each structural retrofit alternative (see detailed explanations in Section 6.2.3). The results are sorted according to the total cost impact potentials in descending order and again discussed.

It can be concluded that alternative HS1 shows by far the most important total cost impact potential in the HDA process among the structural retrofit alternatives because it aims at reducing the *EWC*- and *MVA*-values of hydrogen open path flow O9, O12, and methane cycle path flow C1. Nevertheless, the technical feasibility of a hydrogen/methane-separation method has to be analyzed and the attainable cost savings potential assessed accordingly. Although large investment costs are to be expected the total cost impact

Table 6-5: Total cost impact potentials of the generated structural retrofit alternatives: HDA case study

Label	Structural retrofit alternatives from Table 6-3[a]	Impact on[b]	Energy & waste cost impact potential [kUS$/a]	Material cost impact potential [kUS$/a]	Total cost impact potential [kUS$/a]	Referenced in literature
HS1	Introduce a hydrogen/methane separation method	O9, O12, C1	1100	3690	4790	Referenced[c]
HS2	a) Increase the heat-transfer area in vertex FL b) Use chilled water for vertex FL	O2[d], O3, O5, O6[d], O13, cooling duty of FL	174	92	266	Referenced[e]
HS3	Bypass column DT	O4, cooling duty of DT	31	25	56	
HS4	Introduce a more selective catalyst in reactor RK	O4	2	25	27	

a. The abbreviations refer to the vertices of the process graph in Figure 3-4.

b. The component path flow abbreviations refer to Table 6-2.

c. Kocis and Grossmann (1989) **[37]**

d. Only the *EWC*-value is impacted.

e. Fisher et al. (1987) **[18]**

potential still indicates a fair chance for a good return on investment. Kocis and Grossmann (1989)[37] formulated a MINLP-optimization for the same HDA process and found that the proposed hydrogen/methane-separation method (membrane separation) was part of the final optimal flowsheet structure.

Both options proposed with alternative HS2 aim at reducing the *EWC*- and *MVA*-values of benzene and toluene open path flows O3, O5 and O13. At the same time, methane open path flows O2 and O6 will be partially rerouted from the stabilizing column DS (Figure 3-4) to the gas-cycle purge PU and thus reduce energy costs for cooling in the condenser of that column. Yet, the total cost impact potential for alternative HS2 is probably not high enough to justify an investment to increase the heat-transfer area. Therefore the best option would be to optimize the cooling duty with the presently used coolant as previously discussed. Only if the cost-optimal cooling duty is higher than the cooling capacity of the quench- and flash-unit in the vertex FL a change to a colder coolant (e.g. chilled water) might be considered.

Bypassing distillation column DT (alternative HS3) offers a complete recycling of diphenyl without any related investment costs, yet generates additional energy costs, because diphenyl will consequently accumulate in the liquid cycle path to a level where the reversible formation of diphenyl reaches a thermodynamic equilibrium. The total cost impact potential (third highest potential in Table 6-5) therefore results from the *EWC*- and *MVA*-values of diphenyl open path flow O4 and from the cooling duty requirement in distillation column DT.

Finally, alternative HS4 that also aims at reducing the *EWC*- and *MVA*-values of diphenyl path flow O4 requires investment costs for further catalyst research and will most likely not yield a complete reduction of the diphenyl formation in reactor RK. Owing to the research costs and the lower total cost impact potential in this case it can be concluded that alternative HS3 is preferable to alternative HS4.

In principle, the process improvements through alternatives HS1, HS2 and either HS3 or HS4 can all be carried out simultaneously. Of course, the attainable cost savings potentials need to be determined in a detailed study with the help of a rigorous simulation (and eventually more lab experiments) and have to be checked on their technical feasibility. However, this study is not performed in this thesis.

6.5 Fine Chemical case study

6.5.1 Flow decomposition and assessment results

Table 6-6 shows the results of the assessment procedure applied to the Fine Chemical case study. Again, the path flows are sorted according to ascending *TVA*-values in each path flow category. In this case study no component path flows with *TVA*-value higher than -10 kUS$/a (cut-off value) are displayed.

In the first category, no open path flows with negative *RQ*-values remain after the ranking and cut-off procedure, while *RQ*-values of 0.5 and 0.98 are calculated for the open path flows in the second category of Table 6-6. Although open path flows O1, O3, O5, O6, and O10 have low flow-rates and low *EWC*-values, they nevertheless cause raw material losses while generating little or no output value (negative *MVA*-values) and therefore account for negative *TVA*-values. In turn, the remaining open path flows O2, O4, O7, O8, and O9, with considerably higher flow-rates, show negative *TVA*-values primarily due to high *EWC*-values.

The third and fourth category contain cycle path flows with *RQ*-values greater or equal to zero. In category 3a the cycle path flows of impurity-groups IG1 and IG2 in cycle paths flows C1 and C2 represent the highest flow-rates as well as the most negative *TVA*-values where especially the IG1 path flow exhibits a high *AF*-value (*AF* = 5.7). In Category 3b the only economically important cycle path flow (water flow in C3) holds a negative *RQ*-value.

All cycle path flows in the fourth category generate high *EWC*-values where especially the three reactant R2 cycle path flows have an important impact on the variable process costs. Among the cycle path flows in the fourth category, C4, C5, and C7 have the highest flow-rates (reactants R1 and R2). Albeit a comparably lower flow-rate of R2, cycle path flow C6 however shows the highest specific *EWC*-value in this category (ratio of *EWC*-value per mass flow-rate of a given component path flow), closely followed by reactant R2 cycle path flow C4. All four path flows show the same *RQ*-values while reactant R1 in cycle path flow C7 exhibits by far the highest *AF*-value (*AF* = 45).

Table 6-6: Component path flow assessment results and ranking: Fine Chemical case study

Nr.	**Co.**	**Path**[a]	**Mass Flow**[b] **[-]**	*RQ* **[-]**	*AF* **[-]**	*EWC*[c] **[kUS$/a]**	*MVA*[c] **[kUS$/a]**	*TVA*[c] **[kUS$/a]**
Category 1: Open path flows, $RQ \le 0$								
O1	B	$s_{RK2,\,ir} - d_{RK2,\,or}$	1.5e+1	0	-	1	-150	-151
O2	H_2O	$s_{EX,\,ip} - d_{DH,\,op}$	3.1e+2	0	-	90	-1	-91
O3	IG1	$s_{RK2,\,ir} - d_{EX,\,op}$	2.2e+0	0	-	1	-37	-38
O4	CP	$s_{RK1,\,ir} - d_{DH,\,op}$	8.4e+1	0	-	32	0	-32
O5	R1	$s_{RK2,\,ir} - d_{EX,\,op}$	1.7e+0	0	-	1	-29	-30
Category 2: Open path flows, $RQ > 0$								
O6	R2	$s_{RK2,\,ir} - d_{DH,\,op}$	2.0e+1	0.50	-	8	-202	-210
O7	I	$s_{RK1,\,ir} - d_{RK2,\,or}$	5.0e+2	0.98	-	128	0	-128
O8	R2	$s_{RK2,\,ir} - d_{RK1,\,or}$	2.8e+2	0.50	-	43	0	-43
O9	I	$s_{MI2,\,ip} - d_{RK2,\,or}$	5.2e+2	0.98	-	27	0	-27
O10	R2	$s_{MI1,\,ip} - d_{DH,\,op}$	1.0e+0	0.50	-	0	-10	-10
Category 3: Cycle path flows, $RQ \le 0$								
a) $AF > 1$								
C1	IG1	MI1-DI-DP-MI1	6.9e+1	0	6.7e+0	14	0	-14
C2	IG2	MI1-DI-DH-MI1	2.1e+1	0	1.1e+0	13	0	-13
b) $AF \le 1$								
C3	CP	MI1-DI-DH-MI1	3.2e+0	-0.50	8.2e-3	13	0	-13
Category 4: Cycle path flows, $RQ > 0$								
C4	R2	MI1-DI-DH-MI1	5.1e+2	0.50	5.9e-1	826	0	-826
C5	R2	MI1-DI-DP-MI1	7.7e+2	0.50	1.3e+0	527	0	-527
C6	R2	MI1-DI-DP-DH-EX-MI1	7.5e+1	0.50	4.6e-2	254	0	-254
C7	R1	MI1-DI-DP-MI1	3.3e+2	0.50	4.5e+1	108	0	-108

[a] The abbreviations refer to the vertices of the process graph in Figure 3-6. The descriptions of the cycle paths in Categories 3 and 4 are shortened – only the key vertices to define unambiguously the paths are mentioned.

[b] All mass flow-rates in this column are divided by the smallest component mass flow-rate (O10) – the values are therefore dimensionless

[c] The economic values in these columns are all scaled by a confidential factor.

6.5.2 Identification of optimization parameters and structural retrofit alternatives

Based on the assessment results for the Fine Chemical process, this section discusses in order of ascending *TVA*-values which generic retrofit actions are found to be applicable to the corresponding component path flows. Only path flows with *TVA*-values below -10 kUS$/a are analyzed. After identifying the applicable generic retrofit actions the most important optimization parameters and/or possible structural retrofit alternatives resulting from these are discussed (see Table 6-7). The abbreviations for unit-operations and flowsheet streams of the Fine Chemical process in the discussion refer to the nomenclature used in the process graph of Figure 3-6.

Cycle path flows C4, C5, and C6 of reactant R2 and cycle path flow C7 of reactant R1 all exhibit high *EWC*-values due to their rather high flow-rates. If the optimization/reduction action presented in the fourth category of Table 6-1 is applied, various solutions are formulated that aim at increasing the low equilibrium conversion of the main reaction *(REq. 3-3)* in reactor RK1 (Figure 3-6). Among the optimization variables a variation of the coolant flow-rate to reactor RK1 (indirectly varies the output-temperature in reactor RK1) and a variation of the feed ratio of reactants R1 and R2 (indirectly manipulated by varying the fresh R2 feed-rate to the process $s_{MI1,\, ip}$) is proposed. Alternatively, two structural retrofit alternatives are found to increase the conversion: (i) the cooling system could be modified in order to cool at even lower temperatures or (ii) a different reactor type that reaches higher conversions (e.g. a different catalyst can have effect on the rate of reaction) could be introduced. On the other hand reducing the specific energy consumption (see Table 6-1) for the aforementioned cycle path flows suggests reducing the pressure in all three distillation columns DI, DP, and DH as all of them are operated at pressures above atmospheric level (separation efficiency decreases at higher pressures).

The high specific *EWC*-value of reactant R2 cycle path flow C4 also indicates that rerouting a part (generic retrofit action proposed for the fourth category) of the R2 flow-rate to cycle path flow C5, which shows a notably smaller specific *EWC*-value, is a possible option. This can be performed as

Table 6-7: Applicable generic retrofit actions and resulting optimization parameters as well as structural retrofit alternatives: Fine Chemical case study

Generic action [path flow(s)][a]	Optimization parameters[b] [label][c]	Structural retrofit alternatives[b] [label][d]
• Optimize/reduce the cycle path flow-rates of R2 [C4, C5, C6] and R1 [C7]	• Vary the output-temperature in reactor RK1 (vary the coolant flow-rate) [FP1] • Vary the reactant feed ratio to reactor RK1 (vary the R2 feed-rate $s_{MI1,\,ip}$) [FP2]	• Increase the conversion in reactor RK1 with a new reactor type [FS1] • Introduce a better cooling system for reactor RK1 [FS1]
• Reduce the specific energy consumption of R1 and R2 cycle path flows [C4, C5, C6, C7]	• Vary the pressure of distillation column DI [FP4] • Vary the pressure of distillation column DP [FP7] • Vary the pressure of distillation column DH [FP12]	-
• Reroute (partially) cycle path flow of R2 to cycle path C5 [C4]	• Vary the reflux ratio of distillation column DI to vary the R2 recovery in the distillate while keeping the CP content in the distillate constant [FP3]	-
• Reroute cycle path flow of R2 to cycle path C5 [C6]	• Vary the reflux ratio of distillation column DP to vary the R2 content in the distillate while keeping the P recovery in the distillate constant [FP6]	-
• Optimize/reduce the open path flow-rates of R2 [O6, O10]	• Vary the reflux ratio of distillation column DH to vary the R2 content in the bottom product while keeping the water content in the distillate constant [FP5]	• Use better internals in column DH [FS2] • Introduce a new separation method to remove CP after reactor RK1 [-]
• Remove/reduce the open path flow-rate of B [O1], IG1 [O3], R1 [O5] and IG1 cycle path flow [C1] at the source	• Vary the RK2 reactor pressure [FP9] • Vary the RK2 reactor output temperature [FP8]	• Introduce a more selective catalyst in reactor RK2 [FS3] • Introduce a separation method to partially remove IG1 from external supply $s_{MI2,\,ip}$ [FS5]
• Remove/reduce the water open path flow-rate at the source [O2] and recycle R1 cycle path flow to reactor RK1 [O5]	• Vary the fresh water flow-rate $s_{EX,\,ip}$ to extractor EX [FP11] • Vary the reflux ratio of distillation column DP to vary the R1 content in the distillate while the P recovery in the distillate is kept constant [FP6]	• Introduce a different separation method to purify product P [FS4]

Table 6-7: Applicable generic retrofit actions and resulting optimization parameters as well as structural retrofit alternatives: Fine Chemical case study

Generic action [path flow(s)][a]	Optimization parameters[b] [label][c]	Structural retrofit alternatives[b] [label][d]
• Reduce the *AF*-values of the cycle path flows of IG1 and IG2 [C1, C2]	• -	• Introduce a purge in the cycle path flow C1 [FS6] • Introduce a purge in the cycle path flow C2 [FS7]
• Remove/reduce the cycle path flow-rate of IG2 at the source [C2]	• Vary the output-temperature in reactor RK1 (vary the coolant flow-rate) [FP1]	• Introduce a more selective catalyst for reactor RK1 [FS7] • Introduce a separation method to partially remove IG2 from external supply $s_{MI2,\,ip}$ [FS5]
• Change from the CP cycle to an open path flow [C3]	• Vary the reflux ratio of distillation column DH to vary the CP content in the distillate while keeping the R2 content in the bottom product constant [FP10]	• Use better internals in column DH [FS2] • Introduce a new separation method to remove CP after reactor RK1 [-]

a. Generic actions (Table 6-1) are applied to the component path flow(s) of Table 6-6 in brackets.

b. The abbreviations refer to the vertices of the process graph in Figure 3-6. The component path flow abbreviations refer to Table 6-6.

c. The labels shown in brackets refer to the optimization parameters of Table 6-8.

d. The labels shown in brackets refer to the structural retrofit alternatives of Table 6-9.

described in Table 6-7 by varying the reflux ratio of column DI in order to vary the R2 recovery in the distillate. At the same time, the distillate rate of the column is adjusted to keep the content of coupled product CP constant in the distillate, because CP represents a poison for the solid-bed catalyst in reactor RK2.

The same reasoning and same retrofit action is also applied to the R2 reactant cycle path flow C6. In analogy the reflux ratio of column DP is varied in order to manipulate the R2 recovery in the distillate while the distillate rate itself is adjusted to keep the same product P recovery in the distillate.

Applying the optimization/reduction action (see Table 6-1) to reactant R2 open path flows O6 and O10, that both display negative *TVA*-values in the second category of Table 6-6, leads to various possibilities. The reflux ratio of column DH could be varied in order to manipulate the R2 content in the bottom product while the distillate rate is adjusted to keep the content of coupled product CP in the distillate constant. Among the structural retrofit alternatives, better column internals could be introduced to improve the separation efficiency. As a more radical change, an alternative separation method, instead of distillation columns DI and DH, could be considered to remove coupled product CP from the RK1 reactor output to the necessary degree (e.g. selective absorption for CP, selective CP removal by membrane separation). However, this structural retrofit alternative might also require another separation method to purify product P instead of purification by extraction (EX). The water needed for extraction leaves extractor EX with rather high concentrations of reactants R1 and R2. Before the enriched water phase can be sent to a waste treatment plant the organic loads (reactants R1 and R2) need to be reduced. Yet, the reduction of the R1 and R2 contents is presently performed by distillation column DH. Likewise, these reactants are valuable for the process and could be reused. Hence, if an alternative separation method is introduced after reactor RK1 to remove coupled product CP, a new product purification method might be also needed that does not require water as a mass separation agent. In addition to this, the CP content in the output of reactor RK1 has to be almost totally removed in order to prevent poisoning of the solid-bed catalyst in reactor RK2, which renders the separation task even more difficult. These changes could roughly concern half of the unit-operations involved in the process, so that replacing the entire process plant with a new plant might be more profitable. Therefore, this structural retrofit alternative is not further investigated but could be considered instead for the design of a new plant.

By-product B open path flow O1, impurity-group IG1 open path flow O3, reactant R1 open path flow, and IG1 cycle path flow C1 exhibit negative *TVA*-values that are caused by the side-reactions *(REq. 3-7)*, *(REq. 3-8)*, and *(REq. 3-9)* in reactor RK2. The investigated path flows are attributed to the first category in Table 6-6. If the proposed source reduction action is applied, either the pressure or the feed-temperature of reactor RK2 could be selected as possible optimization parameters. The selectivity could also be improved by developing a better catalyst for reactor RK2. Since impurity-group IG1 is also introduced to the process by external feed $s_{MI2,\ ip}$, the feed could also be pre-purified from IG1 with a new separation method before it enters the process.

Open path flows O2 and O5 (water and reactant R1) also display negative *TVA*-values in the first category of Table 6-6. Applying the source reduction action to water open path flow O2 and the recycling action to reactant R1 open path flow O5 (recycle to reactor RK2), both proposed in Table 6-1 for the first component path flow category, suggests the following alternatives: (i) the fresh water feed-rate to the extractor could be varied, (ii) the reflux ratio of column DP could be varied to manipulate the reactant R1 recovery in the distillate while the product P recovery is kept constant in the distillate, and (iii) a new separation method could be introduced that purifies product P without water as a separating agent and recycles reactant R1.

If the generic retrofit action that aims at reducing the *AF*-values is applied to cycle path flows C1 and C2 of impurity-groups IG1 and IG2 (negative *TVA*-values in Category 3a in Table 6-6) two options arise among the structural retrofit alternatives. The *AF*-value of cycle path flow C1 of impurity-group IG1 could be reduced by introducing a purge into the cycle path flow C1, whereas the *AF*-value of the other cycle path flow C2 of impurity-group IG2 could be reduced by installing a purge in the cycle path flow C2.

Alternatively, the removal/reduction action at the source could be considered with impurity-group IG2 cycle path flow C2. This action could be performed by again indirectly varying the output-temperature of reactor RK1 as described in Table 6-7. Another option would be to introduce a more selective catalyst which would decrease the generation of impurity-group IG2 in reactor RK1. Finally, a separation method to pre-purify the external feed ($s_{MI2,\ ip}$) in which IG2 is also introduced to the process could also be considered to reduce the flow-rate of IG2 in cycle path flow C2.

Finally, because cycle path flow C3 of coupled product CP shows a negative *RQ*-value (Category 3b in Table 6-6), changing the cycle path to an open path is consequently formulated as a possible retrofit action. This leads to various options: (i) the reflux ratio of column DH could be varied to manipulate the CP content in the distillate without changing the R2 content in the bottom product, (ii) better column internals could be used in column DH in order to increase the separation efficiency, or (iii) a new separation method to separate coupled product CP from the reactor RK1 output could be introduced as already discussed in detail before.

6.5.3 Discussion of the identified optimization parameters

The energy cost impact potentials, material cost impact potentials and total cost impact potentials are calculated for the identified optimization parameters and displayed in Table 6-8. Detailed explanations on how to calculate the cost impact potentials are discussed in Section 6.2.3. The results are sorted in descending order according to the total cost impact potentials.

The optimization parameter that scores the highest total cost impact potential in Table 6-8 is the coolant flow-rate to reactor RK1 (parameter FP1). It indirectly manipulates the output-temperature of the reactor. Because the desired reaction is an equilibrium type reaction and the reactor length allows for enough residence time to reach the thermodynamic equilibrium, lowering the output-temperature can therefore increase the conversion. This optimization parameter directly impacts on reactant R2 cycle path flows C4-C6, reactant R1 cycle path flow C7, and possibly also on the generation of impurity-group IG2 by side reaction *(REq. 3-6)* that circulates in cycle path flow C2. Also, since the reaction-rates of the equilibrium reaction decrease at lower temperatures, the fixed residence time in reactor RK1 could prevent the reaction from reaching its chemical equilibrium.

The optimization parameter with the second highest total cost impact potential (parameter FP2) – the variation of the fresh R2 feed-rate $s_{MI1,\,ip}$ that indirectly manipulates the reactant feed-ratio (R1/R2) to reactor RK1 – impacts on the same path flows as parameter FP1 with the exception of impurity-group IG2 cycle path flow C2. As described in the previous section this parameter also influences the conversion in reactor RK1. However, since reac-

Table 6-8: Total cost impact potentials of the identified optimization parameters: Fine Chemical case study

Label	Optimization parameters from Table 6-7[a]	Impact on[b]	Energy & waste cost impact potential [kUS$/a][c]	Material cost impact potential [kUS$/a][c]	Total cost impact potential [kUS$/a][c]
FP1	Vary the output temperature in reactor RK1 (vary the coolant flow-rate)	C4, C5, C6, C7, C2	1728	0	1728
FP2	Vary the reactant feed ratio to reactor RK1 (vary the R2 feed-rate $s_{MI1,\,ip}$)	C4, C5, C6, C7	1715	0	1715
FP3	Vary the reflux ratio of distillation column DI to vary the R2 recovery in the distillate while keeping the CP content in the distillate constant	O7, C4, C5	1481	0	1481
FP4	Vary the pressure of distillation column DI	Reboiler & condenser duties of DI	1290	0	1290
FP5	Vary the reflux ratio of distillation column DH to vary the R2 content in the bottom product while keeping the CP content in the distillate constant	O6, O10, C4	834	212	1046
FP6	Vary the reflux ratio of distillation column DP to vary the R1 and R2 contents in the distillate while keeping the P recovery in the distillate constant	O5, C5, C6, C7	890	29	919
FP7	Vary the pressure of distillation column DP	Reboiler and condenser duties of DP	665	0	665
FP8	Vary the reactor RK2 output temperature	O1, O3, O5, C1, heating & cooling duties of RK2	400	216	616
FP9	Vary the reactor RK2 pressure	O1, O3, O5, C1	17	216	233

Table 6-8: Total cost impact potentials of the identified optimization parameters: Fine Chemical case study

Label	Optimization parameters from Table 6-7[a]	Impact on[b]	Energy & waste cost impact potential [kUS$/a][c]	Material cost impact potential [kUS$/a][c]	Total cost impact potential [kUS$/a][c]
FP10	Vary the reflux ratio of column DH to vary the water content in the distillate while keeping the R2 content in the bottom product constant	O2, O4, C3	135	1	136
FP11	Vary the fresh water flow-rate $s_{EX,\,ip}$ to the extractor EX	O2, O5	91	30	121
FP12	Vary the pressure of distillation column DH	Condenser & cooler duties of DH	32	0	32

a. The abbreviations refer to the vertices of the process graph in Figure 3-6.

b. Refers to the important energy and waste cost sensitive component path flows and the important energy cost sensitive unit-operations. The component path flow abbreviations refer to Table 6-6.

c. The economic values in these columns are all scaled by a confidential factor.

tant R2 is used in heavy excess (R1/R2 feed mass-ratio is approx. 1/3) in order to force a higher thermodynamic equilibrium conversion, the process cost-optimum might not necessarily lie at the highest possible conversion. A cost trade-off can be expected between decreasing variable costs due to a higher conversion and increasing variable costs because of higher reactant cycle path flow-rates.

The variation of the R2 reactant recovery in the distillate of distillation column DI (parameter FP3) is expected to impact mainly on reactant R2 cycle path flows C4 and C5. Probably the recovery of intermediate I in the distillate might be altered as well, if the R2-split between cycle path flows C4 and C5 changes. Therefore the intermediate product I open path flow O7 is included into the total cost impact potential of parameter FP3. However, there is an obvious trade-off between the R2-split between cycle path flows C4 and C5, the recovery of I in the distillate and the reflux ratio without changing the content of coupled product CP in the distillate. Thus, this parameter might have a much lower total cost impact potential than calculated and might also behave in a non-linear fashion.

A variation of the pressure in distillation column DI (parameter FP4) mainly aims at reducing the energy consumption of that unit-operation with probably little effect on involved path flows if the separation efficiency is held constant. The total cost impact potential is then calculated with the utility costs for heating and cooling in the reboiler, condenser, and bottom-product after-cooler. The same reasoning also holds for the variation of the pressure in distillation columns DP (parameter FP7) and DH (parameter FP12). The total cost impact potential for the latter parameter is calculated in a slightly different manner. A reduction of the reflux ratio in column DH also decreases the vapor overheads (containing mainly reactant R2) that are partially used to heat distillation columns DI and DP. For this reason the net steam cost impact is virtually zero. Only the condenser duty required for the unused overheads of column DH and the cooling duty of the bottom-product cooler in vertex DH are mainly impacted. The total cost impact potential for this optimization parameter accordingly scores last priority.

The next optimization parameter in Table 6-8 (parameter FP5) – the variation of the R2 content in the bottom product in distillation column DH while the content of coupled product CP in the distillate is kept constant – mainly influences reactant R2 open path flows O6, O10, and reactant R2 cycle path flow C4. A trade-off between cycle path flow C4 and open path flows O6/O10 is expected. A similar variation in distillation column DP (parameter FP6) as described in Table 6-8 mainly impacts on reactant R1 open path flow O5, reactant R2 cycle path flows C5 and C6, and reactant R1 cycle path flow C7. A trade-off between these path flows and the reflux ratio is also expected here. In analogy to the optimization parameter of parameter FP3, the total cost impact potentials for parameters FP5 and FP6 could therefore be lower than calculated and the investigated parameters could behave in a non-linear manner. Further, the contents of R1 and R2 cannot be reduced below an existing

P/R2-azeotrope. This indicates that parameter FP6 will probably exhibit a strongly non-linear cost sensitivity.

Varying the pressure and output-temperature of reactor RK2 (parameters FP8 and FP9) in order to influence the selectivity of the undesired side-reactions *(REq. 3-7)*, *(REq. 3-8)*, and *(REq. 3-9)* should mostly influence by-product B open path flow O1, impurity-group IG1 open path flow O3 and cycle path flow C1, as well as reactant R1 open path flow O5. The temperature variation will also impact on the external heating and cooling requirements for reactor RK2. It is probable that both parameters cannot be varied in a broad range without affecting the conversion of the main reaction *(REq. 3-4)*. If the pressure is lowered too much the necessary production capacity might not be met. The pressure cannot be increased too high either because of pressure limits on the equipment side. In either case both parameters cannot be included in a process optimization since no kinetic model is available to describe the main and side-reactions in reactor RK2.

The variation of the reflux ratio in distillation column DH can also be used to manipulate the content of coupled product CP in the distillate when the R2 reactant content in the bottom product is held constant (parameter FP10). Mostly water open path flow O2, open path flow O4 and cycle path flow C3 of coupled product CP are affected by this optimization parameter. For similar reasons, as described with parameters FP3, FP5, and FP6, a trade-off between the open path flows, the cycle path flow and the reflux ratio is expected. Therefore, the total cost impact potential might be much lower than calculated in Table 6-8. It is also possible that the parameter might behave in a non-linear fashion.

Finally, varying the fresh water flow-rate $s_{EX,\,ip}$ for extractor EX (parameter FP11) is expected to mainly influence water open path flow O2 and reactant R1 open path flow O5. Reactant R2 is very soluble in water and will probably not be affected. This optimization variable is constrainted by the quality specifications for the final product stream $s_{EX,\,op}$. The minimum purity for product P is required while the concentration of reactant R1 is not allowed to exceed 1 wt%. The fresh water stream thus cannot be lowered so that one of these specifications are not met.

6.5.4 Discussion of the generated structural retrofit alternatives

The energy cost, material cost and total cost impact potentials are calculated for the generated structural retrofit alternatives and displayed in Table 6-9. Detailed explanations on how to calculate the cost impact potentials are discussed in Section 6.2.3. The results are sorted in descending order according to the total cost impact potentials.

The structural retrofit alternative that targets by far the highest total cost impact potential is alternative FS1. An improvement of the conversion in reactor RK1 can considerably reduce the flow-rates in reactant R2 cycle path flows C4, C5, and C6 as well as in reactant R1 cycle path flow C7. Of course the temperature of the cooling system could be modified or exchanged in order to lower the output-temperature in reactor RK1 and subsequently increase the conversion. Unfortunately, the kinetics would also slow down so that the residence time in the reactor would have to be further extended. In a plug-flow reactor system – as presently used – this requires a longer reactor to reach the thermodynamic equilibrium. This problem could be solved if an appropriate catalyst was found to accelerate the kinetics accordingly. The other possibility lays in separating either water or intermediate product I directly from the reactor to force the equilibrium on the product side and thus increase the conversion. This could be done in a reactor-separation cascade or even continuously.

Using more efficient column internals in distillation column DH (alternative FS2) mainly taps the *TVA*-values of reactant R2 open path flows O6, O10, and cycle path flow C3 of coupled product CP. It also taps the energy cost requirements of the condensation of the unused vapor distillate (heat integration) and the costs for the cooling of the bottom product of distillation column DH as already discussed in detail in the previous section in alternative FP12. Although the total cost impact potential is already much lower than calculated for alternative FS1 it remains an interesting alternative. However, only a part of the calculated total cost impact potential is expected to be realized,

Table 6-9: Total cost impact potentials of the generated structural retrofit alternatives: Fine Chemical case study

Label	Structural retrofit alternatives from Table 6-7[a]	Impact on[b]	Energy & waste cost impact potential [kUS$/a][c]	Material cost impact potential [kUS$/a][c]	Total cost impact potential [kUS$/a][c]
FS1	Introduce a new reactor type in RK1 or improve its cooling system to increase the conversion	C4, C5, C6, C7	1715	0	1715
FS2	Use better internals in column DH	C3, O6, O10, cond. and cooling duty of DH	54	212	266
FS3	Introduce a more selective catalyst for reactor RK2	O1, O3, O5, C1	13	216	229
FS4	Introduce a different separation method to purify product P	O2, O5[d]	90	30	120
FS5	Introduce a separation method to part. remove IG1 and IG2 from external supply $s_{MI2, ip}$	C1, C2, O3	28	37	64
FS6	Introduce a purge in the cycle path MI1-DI-DP-MI1	C1	14	0	14
FS7	Introduce a purge in the cycle path MI1-DI-DH-MI1 or introduce a more selective catalyst for reactor RK1	C2	13	0	13

a. The abbreviations refer to the vertices of the process graph in Figure 3-6.

b. The component path flow abbreviations refer to Table 6-6.

c. The economic values in these columns are all scaled by a confidential factor.

d. Only the MVA-value is used for the material cost impact potential.

since the separation efficiency of the column trays probably cannot be increased dramatically. On the other hand, investment costs for different column internals are also relatively low.

The structural retrofit alternative with the third highest total cost impact potential is found to be an improvement of the selectivity of the solid-bed catalyst in reactor RK2 (alternative FS3). Ideally, a more selective catalyst could tap the cost impact potential in by-product B open path flow O1, impurity-group IG1 open path flow O3 and cycle path flow C1, as well as reactant R1 open path flow O5. However, the postulated reaction *(REq. 3-8)* indicates the formation of impurity-group IG1 from impurity-group IG2. If the selectivity of the catalyst is improved so that the generation of IG1 is decreased, impurity-group IG2 will build-up to a higher degree in the process and would increase the energy-costs at the same time.

Alternative FS4 – introducing a different separation method to purify product P instead of extractor EX – aims at reducing the *TVA*-value of water open path flow O2 and the *MVA*-value of reactant R1 open path flow O5. The *EWC*-value of the latter path flow is not expected to decrease because recycling R1 would certainly increase the energy costs in the process. The total cost impact potential of alternative FS4 ranks fourth priority in Table 6-9. Even though the mass separation agent (water) introduces energy and disposal costs to the process, the extraction itself still consumes virtually zero variable costs (electricity for the rotating discs used in the column). Therefore, given the relatively low total cost impact potential, it will be difficult to find an alternative separation method with an adequate return on investment.

The next structural retrofit alternative in Table 6-9, alternative FS5, targets the cost impact potentials in impurity-group IG1 cycle path flow C1, impurity-group IG2 cycle path flow C2, and impurity-group IG1 open path flow O3. Both impurity-groups are not only generated in the process but also fed to the process in external supply $s_{MI2,\,ip}$. Pre-purifying that feed can therefore reduce the flow-rates in the aforementioned path flows and consequently reduce their *EWC*-values. Savings in the *MVA*-value of the open path flow O3 is also expected because impurity-group IG1 is postulated to be generated in the consecutive reactions *(REq. 3-6)* and *(REq. 3-8)* from reactant R1. Subsequently, R1 is lost in the formation of IG1 and leaves the process in open path flow O3. The total cost impact potential as calculated in this manner is rather low and assigns fifth priority to this alternative in Table 6-9. Nevertheless, the attainable total cost impact potential could be considerably different than calculated, because it is unclear if the impurity-groups have a positive or negative effect on the separation efficiencies of the three main distillation columns DI, DH, and DP. In either case a rigorous simulation is needed (and eventually lab experiments) to further investigate alternative FS5.

The last two alternatives FS6 and FS7 in Table 6-9 – introducing a purge into cycle path flows C1 and C2 respectively – aim at reducing the accumulation factors in both cycle path flows. The total cost impact potentials of these alternatives are due to the *EWC*-value of either cycle path flow and score the lowest priorities accordingly. Obviously, the same reasons as discussed with alternative FS5 could lead to widely different total cost impact potentials which makes a detailed analysis with the help of a rigorous simulation necessary. A trade-off between the purging of valuable components in both purges on the one hand and on the other hand the reduction of the accumulation factors of both impurity-groups is probable. The cost-optimum purge flow-rate therefore has to be determined for both alternatives. Moreover, the purge streams could be disposed of in an incineration facility which might even return steam credits for both purge streams (presently only steam is produced by incineration). However, this is highly dependent on the remaining capacity of that incineration facility. If no extra capacity is left, disposal costs might have to be paid.

Alternatives FS1 and FS2 can be carried out simultaneously because they do not tap common cost impact potentials. Alternatives FS3 – FS7 target the removal of impurity-groups and by-products in the process. More specifically, alternatives FS3 and FS4 aim at reducing the formation of impurity-groups and by-products at the source, while alternatives FS5 or the combination of FS6 and FS7 are two possible options to decrease the flow-rates of the impurity-groups building up in the recycles or directly introduced by the external supply $s_{MI2,\,ip}$. Therefore a slight overlap between both types of strategies can be expected. It has also to be decided if either alternative FS5 or the combination of alternatives FS6 and FS7 is to be applied. The purge alternatives FS6 and FS7 will probably remove the impurity-groups IG1 and IG2 less effectively than alternative FS7 but however also at much lower investment costs.

6.6 Discussion and conclusions

6.6.1 The significance of a total cost impact potential

The total cost impact potential, calculated for identified optimization parameters, is not intended as a cost reduction target, but merely indicates the impact magnitude of the investigated parameter on the energy and material costs of the process. More precisely it indicates the cumulated "leverage effect" or cost effect of each identified optimization parameter on the variable process costs. Usually, varying a process parameter will have an effect on the manipulated unit-operation itself and on several component path flows. In many cases those effects show cost trade-offs where an optimum value is desirable. Yet, it is quite difficult to estimate without rigorous simulation to what extent each effect contributes to the cost trade-off. Therefore, no attempt is made to estimate the extent of each effect nor the direction of the cost-gradient relatively to the direction in which the investigated parameter is varied. The total cost impact potential merely sums the different *EWC*-values and *MVA*-values of the path flows or the energy costs of the unit-operations in the base case affected by the optimization parameter. This procedure is chosen because it is assumed that the higher the total cost impact potential is, the higher the chance is that the investigated optimization parameter plays an important role in the process optimization. This can be useful for pre-selecting important operating parameters that are to be included in a process optimization.

The total cost impact potential of a structural retrofit alternative on the other hand serves as an economic performance indicator to estimate the order of magnitude of the variable cost savings to be expected and to rank them among other structural retrofit alternatives relative to each other. The interpretation of the meaning of an impact potential for a structural retrofit alternative is different as compared to an optimization parameter. This is due to the fact that in case of structural retrofit alternatives the direction of the effects on component path flows and unit-operations can be predicted more easily since these are actually intended to "break" trade-offs in the process. The rough evaluation procedure is useful if only a limited amount of time is available in order to decide which of the generated structural retrofit alternatives is to be further analyzed in a detailed study. Similarly, the calculation procedure forces the user to reflect upon the process changes introduced by the investigated structural alternative and possibly contributes to a better process understanding at the same time. However, the attainable cost savings potential cannot be determined without using a rigorous process simulation. In some cases the attainable cost savings potential will be much lower than the calculated one, if e.g. constraints in the process are soon reached and cannot be removed easily. In other cases the attainable potential might even be much higher than the calculated one, because of non-linear effects in the process. Besides, due to the manner in which the total cost impact potential is calculated, energy costs caused by a given unit-operation can sometimes occur twice – e.g. partially in the *EWC*-value of a component path flow and completely as energy cost requirement of the unit-operation. Even if this inaccuracy can be expected, the total cost impact potential of a structural retrofit alternative is only intended to indicate the order of magnitude of the maximum possible variable cost savings.

6.6.2 Additional aspects on the generation of retrofit options

In a systematic sensitivity analsis of the optimization parameters, that are identified to be of major importance for the investigated process, parameter variations are often found to be constrained by equipment capacity bottlenecks. If a parameter variation beyond such a constraint further increases the overall economic performance, either new unit-operations might be required or the constraining unit-operations might have to be modified. Some of these new structural retrofit alternatives can be found before a sensitivity analysis is carried out, if general engineering knowledge is used to reflect on the process changes induced by a given parameter variation. Others might only be discovered if a sensitivity analysis is performed. However, only a process cost optimization on a rigorous process simulation model can indicate which parameter changes are really optimal.

It should be noted that the presented approach for generating retrofit options does not consider heat integration but aims at reducing process energy requirements. Douglas (1985)[12] stated that decisions in process design necessarily follow a hierarchical order in which he considers heat integration or decisions in the utility system after decisions at the reaction and separation level are made. Although the task separation of reducing process energy requirements before considering heat integration measures might not always be the best solution, it considerably reduces the complexity in retrofitting. Therefore, the author proposes to analyze heat integration potentials only after the best retrofit alternatives have been determined and applied to the investigated process.

6.6.3 Case study results

The application of the presented method to the HDA case study demonstrates the capacity of the method to find important optimization parameters and to generate structural retrofit alternatives. The same optimization parameters as explicitely cited by Fisher et al. (1987)[18] are found and the conversion and purge parameter also turn out to be by far the most relevant ones. Among the structural retrofit alternatives the hydrogen/separation alternative (alternative HS1 – Table 6-5) yields the highest total cost impact potential and is also part of the final MINLP cost-optimized flowsheet structure described by Kocis and Grossmann (1989)[37]. Alternative HS2 (see Table 6-5), either increasing the heat exchange area in vertex FL or introducing a better cooling utility, is equally proposed by Fisher and co-workers. Only the necessity of increasing the CO compressor capacity as a result of an optimized gas recycle flow-rate $f_{PU,\,CO}$ (see Figure 3-4) is not discovered at this level of the method. However, this would certainly show up once a sensitivity analysis and a subsequent process optimization has been performed.

The findings for the Fine Chemical case study cannot be compared to the existing literature for obvious reasons. However, among the structural retrofit alternatives the introduction of a new reactor type instead of reactor RK1 as well as an improved cooling system (both alternative FS1 in Table 6-9) were already proposed by the engineers in charge of the existing process plant and investigated in great detail. Research on a more selective catalyst for reactor RK2 (alternative FS3) has been carried out quite intensively up to now, a new purge was recently introduced into the cycle path flow C2 (alternative FS7), and more efficient column internals in the top segment of distillation column DH (alternative FS2) were investigated as possible retrofit projects. A separation method to pre-purify the external supply $s_{MI2,\, ip}$ (see Figure 3-6) from the impurity-groups (alternative FS5) was also considered but not recently investigated in detail. Finally, a different method to purify product P (alternative FS4) and a new purge in the cycle path flow C1 (alternative FS6) have not yet been formulated to the knowledge of the author.

No parameter optimization has been carried out for the entire process plant of the Fine Chemical case study yet. However, a list of recommended value ranges for important parameters exists for the investigated process. Nevertheless, based on these value ranges, the author concludes that the optimization parameters FP1, FP2, FP4, and FP7 can be considered to be of major importance.

7 EVALUATION OF OPTIMIZATION PARAMETERS: FINE CHEMICAL CASE STUDY

7.1 Description of the evaluation procedure

In this chapter the optimization parameters of the investigated process that were identified to be of major importance in **Step 5** of the screening method (see Figure 2-3) are evaluated in more detail in **Step 6** according to the procedure shown in Figure 7.1.

At the beginning the selected optimization parameters are varied in a local sensitivity analysis. Moreover, the results of the sensitivity analysis are subsequently used to perform a parameter optimization in order to minimize the variable costs (raw materials, waste disposal, electricity, cooling water, and steam) of the investigated process. If a parameter variation is limited by equipment or other contraints in the sensitivity analysis and important cost sensitivities hint at further cost savings by removing these constraints, new structural retrofit alternatives can be formulated and are then further investigated in the following chapter. The evaluation procedure is demonstrated on the Fine Chemical case study. The minimization of variable process costs is chosen as objective function throughout the evaluation procedure.

7.2 Introduction to sensitivity analysis and parameter optimization

7.2.1 Sensitivity analysis in process flowsheet simulators

Sensitivity analysis consists in analyzing the response of *dependent variables* of a process to a change of a single *problem variable* (*local* sensitivity analysis) or to a simultaneous change of multiple *problem variables* (*global* sensitivity analysis). Problem variables physically represent equipment specifications and operating conditions (e.g. pressures, temperatures, feed-rates). One major advantage of process flowsheet simulators is the possibility to perform sensitivity analysis directly on a process simulation model. In equation-oriented process flow-

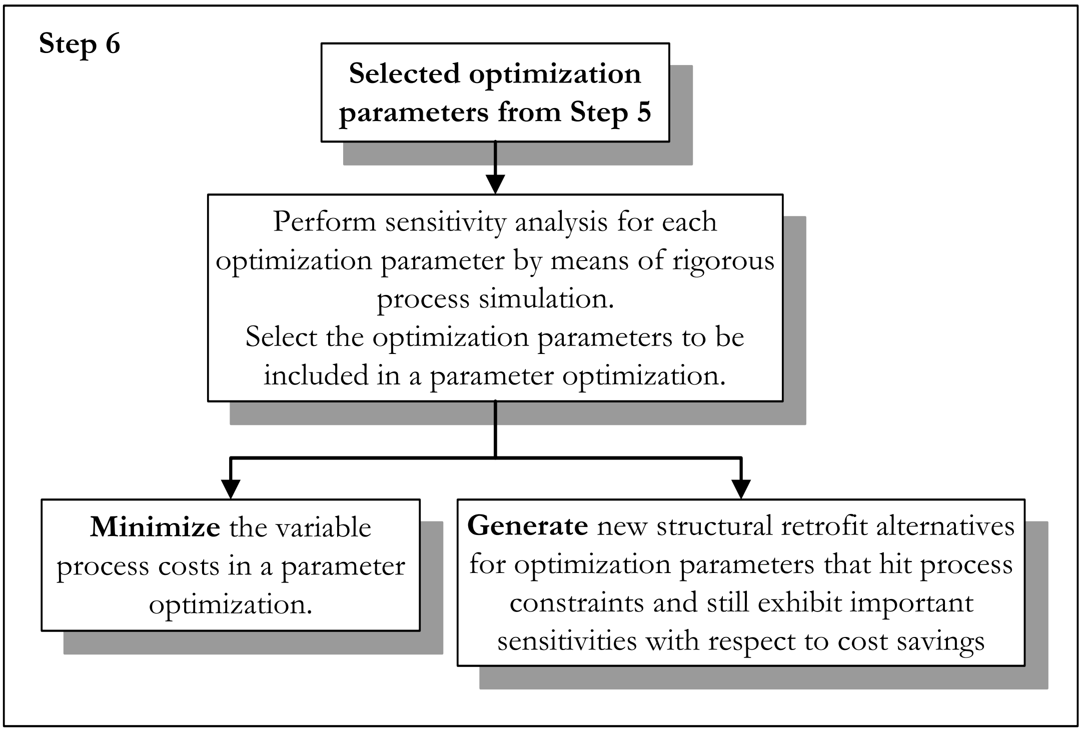


Figure 7-1: Evaluation procedure in Step 6 for identified optimization parameters (refers to the master scheme of the screening method in Figure 2-3)

sheet simulators (see Section 3.3) the user has access to the model equations. Thus, sensitivities can be determined analytically from the gradients of the overall function that defines the dependent variable of interest. In sequential modular process flowsheet simulators, the model equations inside the unit-operations are most often not accessible. Therefore problem variables have to be *perturbed* around their base case values and the corresponding operating steady-states of the process model have to be calculated at each perturbation accordingly. As the commercial flowsheeting software package Aspen Plus® that is used to simulate the Fine Chemical process is a sequential modular process flowsheet simulator, the sensitivity analysis is carried out by simulating the new steady-state of the process model after each perturbation step of a problem variable.

7.2.2 Parameter optimization in process flowsheet simulators

In practical terms, optimization is performed on a given process in order to quantify its “best solution” with respect to a quantitative performance measure – the *objective function*. Typical objectives for process optimization include e.g. the minimization of process capital costs in the design phase and the minimization of variable process costs during the operation phase. The values of the objective function are determined by manipulation of the problem variables. Further, the limits of process operation, product quality specifications, process safety limits, and relationships between the problem variables need to be considered as *constraint equations*. In a process flowsheet simulator the constraint equations are included in the process simulation model itself. Problem variables are further classified into *decision variables* that represent degrees of freedom in the optimization and dependent variables that can be solved from the constraint equations.

Often, the optimization problem for a chemical process has a non-linear objective function and/or non-linear constraint equations of the problem variables and is referred to as *non-linear program*. The solution of this kind of optimization problems is referred to as *non-linear programming* (NLP). In addition, the optimization problem becomes considerably more difficult if problem variables are included that take only integer values. These problems are referred to as *mixed integer non-linear programs* (MINLPs). In this thesis, the Fine Chemical process optimization only concentrates on problem variables that can be varied continuously in a region (process operating parameters) and can thus be solved by non-linear programming. Therefore, the process optimization is later referred to as *parameter optimization*. There are numerous algorithms to solve non-linear problems in both sequential modular and equation-oriented process flowsheet simulators. Successive Quadratic Programming (SQP) is one of the most frequently used algorithms in both types of simulators as it requires far fewer calculation steps than other well-known methods (Biegler et al. (1997)[5]). The SQP-algorithm is implemented in the Aspen Plus® flowsheeting software package and is used for the parameter optimization.

7.3 Simulation models for evaluating optimization parameters

Two different models containing minor modifications as compared to the previously described base case model (Section 3.5.2) are used for the evaluation of the optimization parameters of the Fine Chemical case study that were identified to be of major importance:

- A *sensitivity model* that does not take the impurity-groups IG1 and IG2 into account but that includes a design specification to keep the P product production rate of the base case model constant in each variation.
- An *optimization model* that corresponds to the base case model and that also includes the design specification to keep the desired production rate of product P constant.

7.4 Sensitivity analysis

7.4.1 Implementation of the sensitivity analysis

In Section 6.5 twelve optimization parameters have been identified to be of major importance with regard to the economic performance of the Fine Chemical case study. As mentioned in Section 6.5 the RK2 reactor (see Figure 3-6) pressure and temperature (parameters FP8 and FP9 – see Table 6-8) cannot be varied because no reaction kinetics are available for the main reaction *(REq. 3-4)* in reactor RK2.

The selected optimization parameters (problem variables) are varied in a local sensitivity analysis by a maximum of ± 40% as compared to their base case values. Most parameters are however varied in a smaller range because process constraints are either encountered earlier or costs increase dramatically. For each optimization parameter approximately 6-8 values above or below its base case value are simulated (perturbation steps). In the following sections each variation of an optimization parameter is discussed in an individual section. The abbreviations used for the unit-operations always refer to the process graph in Figure 3-6. The “constraint” indications inside the following sensitivity figures (Figure 7-2 - Figure 7-12) indicate known or calculated process constraints either due to equipment capacity limitations or process quality specifications.

7.4.2 Description of the sensitivity model

The variable costs of the process (raw materials, waste disposal, electricity, cooling water, steam) serve as the objective function to measure the cost difference to the costs of the base case model. The differences of the sensitivity model to the base case model are explained in the following paragraphs.

The production flow-rate $d_{EX,\,op}$ that contains >95 wt% of product P needs to remain constant in each simulation of the local sensitivity analysis. However, the variation of a single optimization parameter in a sensitivity simulation indirectly affects this production flow-rate. Since R2 is the reactant used in excess (to increase the equilibrium conversion in reactor RK1 – see Figure 3-6) the R1 reactant feed-rate to the process in $s_{MI1,\,ip}$ (Figure 3-6) controls the overall production flow-rate and is adapted accordingly in each sensitivity simulation. The energy credits from the combustion of the organic wastes of all site production facilities (generation of mid pressure steam and reuse of the remaining heat in the combustion gases – see Section 3.5.2) are fixed in the sensitivity model. However, when an optimization parameter is varied in the sensitivity analysis the organic waste loads of the investigated process change accordingly. Nonetheless, this change is not taken into account because the organic waste loads from the investigated process are comparably small.

In order to simplify the convergence in each sensitivity simulation the impurity-groups IG1 and IG2 are not included into the sensitivity model – i.e. the side reactions *(REq. 3-6)*, *(REq. 3-8)*, and *(REq. 3-9)* are not taken into account as well as the external feed $s_{MI2,\,ip}$ of both impurity-groups.

The distillation columns are generally set up with individual component murphree efficiencies of approximately 0.6 in the optimization model. Unfortunately, the lack of impurity-groups in the sensitivity model leads to lower reflux-ratios in the distillation columns DH and DP (see Figure 3-6) and slightly different separation profiles than measured in the mass and energy balances of the existing plant. In fact the impurity-groups render the separation tasks in these columns more difficult. Therefore, the individual component murphree efficiencies in both columns are slightly modified so that the calculated results of the sensitivity model approximately match the measured mass balances of the main components in the base case model.

7.4.3 Reactor RK1 outlet temperature (FP1)

As discussed in Sections 6.5.2 and 6.5.3 the outlet temperature of reactor RK1 influences the equilibrium conversion of its main reaction *(REq. 3-3)*. The temperature itself can be manipulated by the coolant flow-rate to the reactor system. The results of the sensitivity analysis for this optimization parameter are shown in Figure 7-2.

The coolant flow-rate is varied by ±3% of its base case value, which yields a variation of the outlet temperature of ±1.2%. The difference in total costs in turn varies by roughly ±2%. Figure 7-2 shows that the total costs decrease if the coolant flow-rate is increased to reach lower reactor outlet temperatures. In the investigated range the total costs are approximately linearly proportional to the reactor outlet temperature. The conversion of the main reaction in reactor RK1 follows the same trend and varies by ±5% of its base case value. The total cost savings are dominated by the steam savings that are in turn mostly caused by a reduction of the energy requirements for distillation columns DH and DI. The raw material, waste disposal, electricity, and cooling water costs are much less sensitive to the parameter variation. As can be expected the electricity costs increase slightly because more coolant is required (compression-type cooling system).

7.4.4 Reactant R1/R2 feed mass-ratio to reactor RK1 (FP2)

The R1/R2 reactant feed mass-ratio at the inlet of reactor RK1 also influences the equilibrium conversion of the main reaction *(REq. 3-3)*. This ratio is directly controlled by fresh reactant R2 feed $s_{MI1,\,ip}$ to the process. A higher

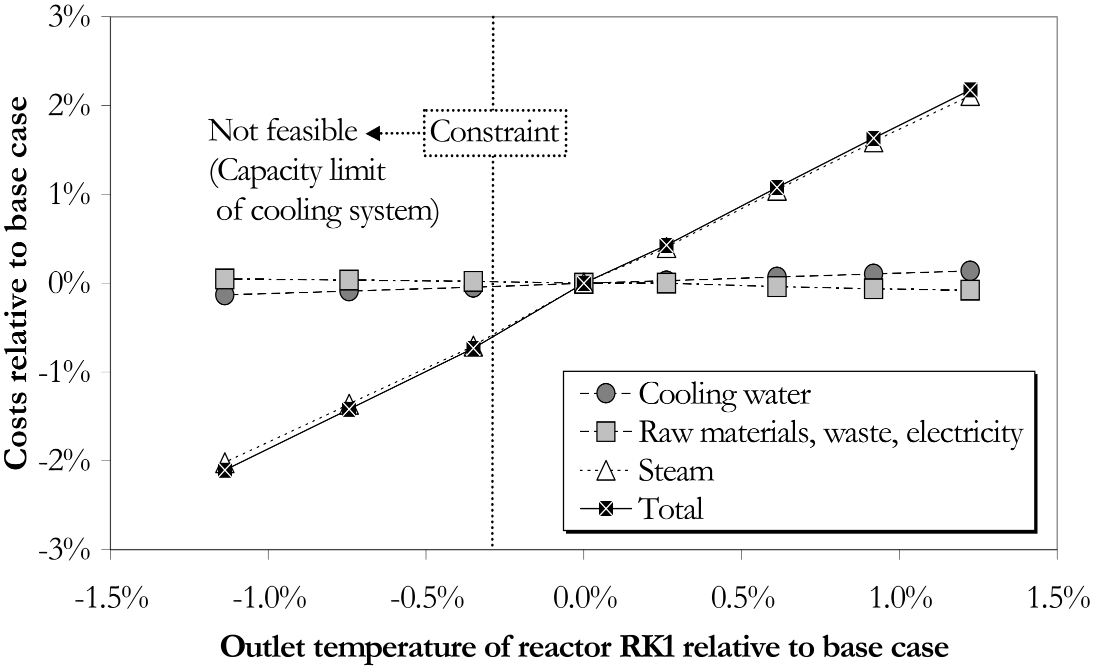


Figure 7-2: **Sensitivity analysis of the outlet temperature of reactor RK1 with regard to variable costs**

fresh reactant feed decreases the ratio whereas a lower feed increases it. The cost sensitivity of this parameter variation is shown in Figure 7-3.

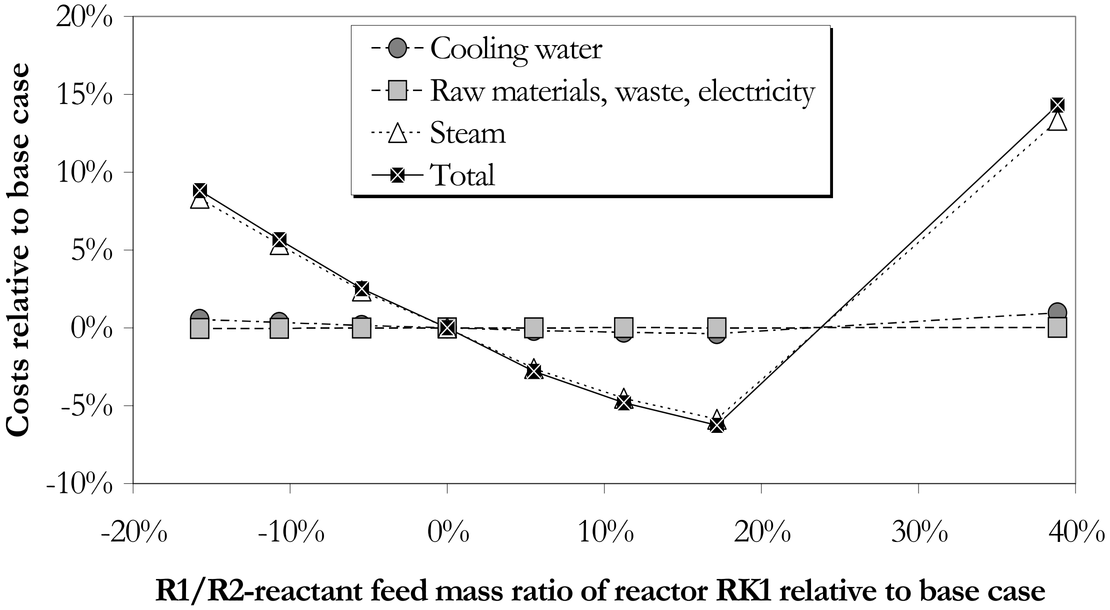


Figure 7-3: **Sensitivity analysis of the R1/R2-reactant feed mass-ratio of reactor RK1 with regard to variable costs**

The fresh R2 reactant feed-rate is varied from -10% to +4% of its initial base case value which causes the R1/R2 feed mass-ratio to vary from from -16% to +38% relative to its base case value. In the direction of an increasing ratio, the reactor conversion first increases to a maximum of +6% of the base case value and then drops again to -6%. In the opposite direction the conversion decreases directly to -4% of the initial value.

The resulting total costs vary considerably between -7% to +15% of the base case costs. The total cost curve itself indicates a cost minimum at the reactant ratio of +17% and exhibits a higher-order proportionality to the reactant ratio. As in the previous section the total costs are heavily influenced by the steam costs because the other cost categories are far less sensitive. The cooling water costs follow the same trend and also go through a minimum. The combined curve that indicates the cost variation of the raw materials, the waste, and the electricity consumption instead has an inverted shape and exhibits a cost maximum. The raw material costs dominate this curve and are mostly caused by the change of the fresh R2 reactant feed-rate. Further, the steam and cooling water costs mainly result from changing utility requirements in distillation columns DH and DI.

7.4.5 Reactant R2 recovery in the overheads of column DI (FP3)

Reactant R2 is an intermediate key component in distillation column DI. About 61% of the total R2 reactant feed to the column is recovered in the overheads in the base case model. The separation task consists in recovering almost 100% of the generated intermediate product I from reactor RK1 in the overheads, while almost all of coupled product CP is separated to the bottom product. The R2 reactant recovery in the overheads can be varied by manipulating the column reflux ratio. The results of the sensitivity study on this optimization parameter are displayed in Figure 7-4.

The reflux ratio is varied from +1.5% to -0.2% of its base case value which causes the R2 reactant recovery to vary from -12% to +5% – the base case being 61% R2 recovery in the distillate. In parallel the content of coupled product CP in the overheads is kept constant at the base case value by adjust-

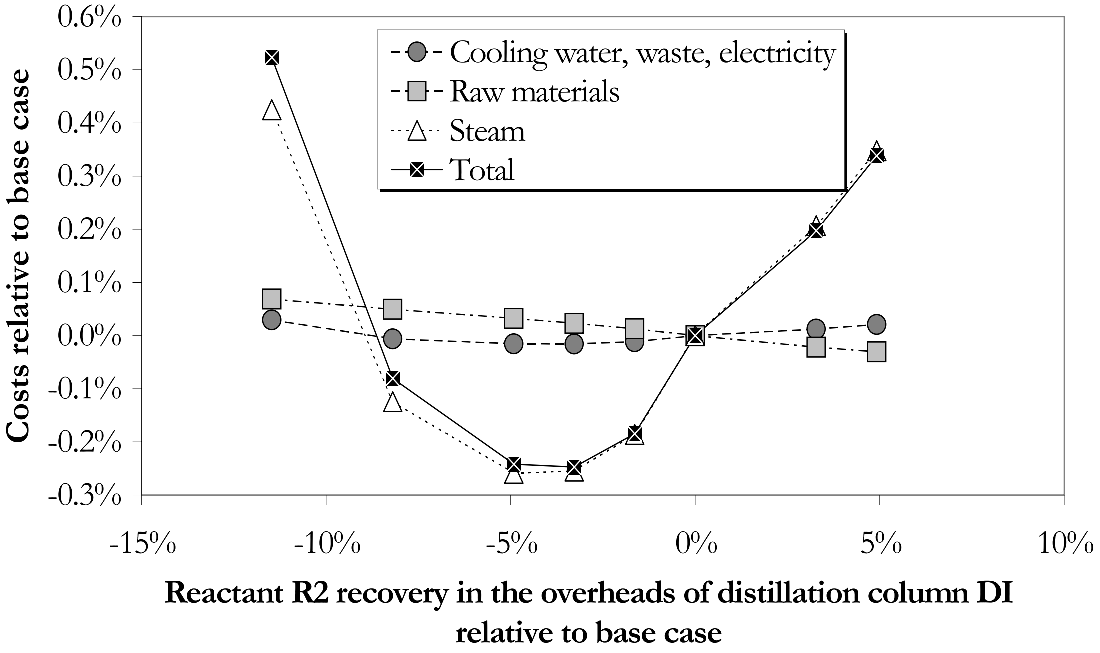


Figure 7-4: Sensitivity analysis of the reactant R2 recovery in the overheads of distillation column DI with regard to variable costs

ing the distillate rate of the column. In response the total costs vary roughly from -0.25% to +0.5% relative to the base case in the investigated interval which indicates a relatively week sensitivity. In the direction of decreasing R2 recoveries the total costs first decrease as well, then stay constant in a minimum, and finally increase rapidly again. In the opposite direction the total costs only increase. Therefore, the total costs are clearly non-linearly proportional to the reflux ratio.

Not surprisingly are the total costs again mostly dominated by the steam costs which display a similar trend. Two different trends that cause the specific curve shape can be observed. If the R2 recovery is decreased, the energy requirement of the steam reboiler of distillation column DI decreases, even though the reflux ratio increases. At the same time the steam requirements in the reboilers of the other distillation columns DH and DP, nevertheless increase. The raw material, waste, electricity, and cooling water costs are much less sensitive than the steam costs. The cooling water costs dominate the combined cost curve in Figure 7-4. The raw material costs are almost solely influenced by the costs for fresh reactant R2 from supply flow $s_{MI1,\, ip}$. These increase when the R2 recovery is decreased.

7.4.6 Pressure in distillation column DI (FP4)

The pressure in distillation column DI affects its separation efficiency. In the base case the absolute column pressure is set to approximately 2.0 bar in the reboiler. This optimization parameter is varied from -20% to +15% (1.6 bar to 2.3 bar) of the base case value, which causes the total costs to vary from -3.5% to +2.8%. The resulting costs curves are shown in Figure 7-5.

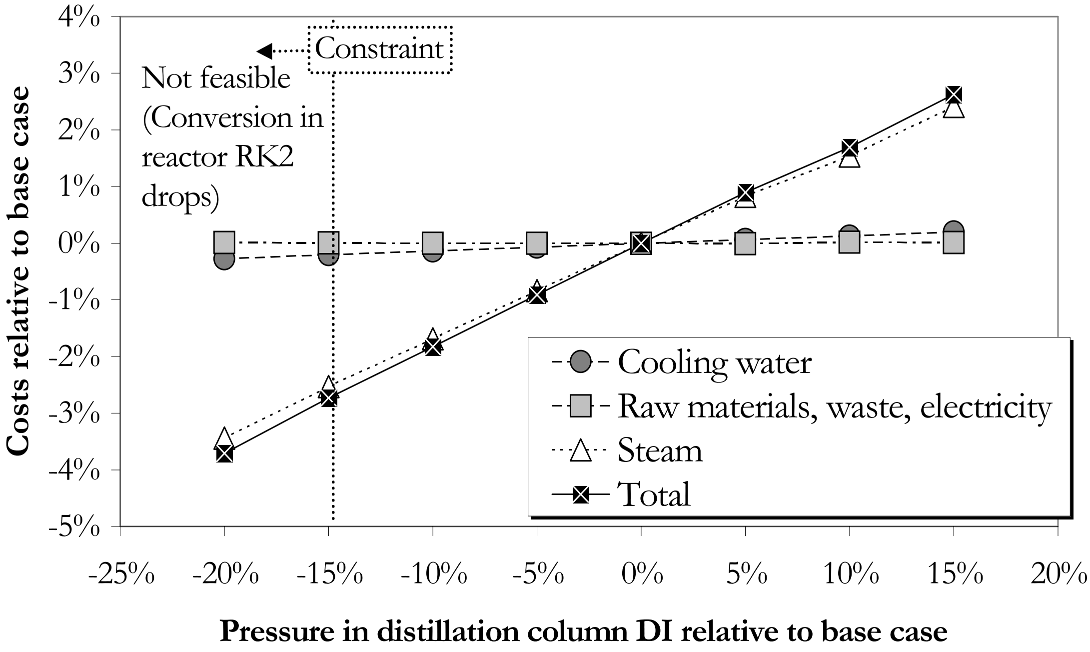


Figure 7-5: Sensitivity analysis of the pressure in distillation column DI with regard to variable costs

The total and the steam cost curves exhibit a linear proportionality to the pressure in the investigated interval. The total costs are mostly influenced by the steam costs because the sensitivities of the cooling water, raw material, waste, and electricity costs are rather weak compared to the sensitivity of the steam costs. The combined cost curve in Figure 7-5 is mostly dominated by the raw material costs in the same manner as described in the previous section. As expected, a pressure reduction decreases not only the steam consumption in the distillation column DI but also the necessary cooling duties. The pressure variation has almost no effect on the other energy requirements of other unit-operations.

7.4.7 Reactant R2 content in the bottom product of distillation column DH (FP5)

The separation in distillation column DH yields almost all of the CP coupled product and a reactant R2 content of 1 wt% in the bottom product in the base case. This optimization parameter can be controlled by manipulating the column reflux ratio. The reflux ratio itself is varied from +3% to -2%. This causes the R2 content to vary by ±30% relative to the base case content as displayed in Figure 7-6.

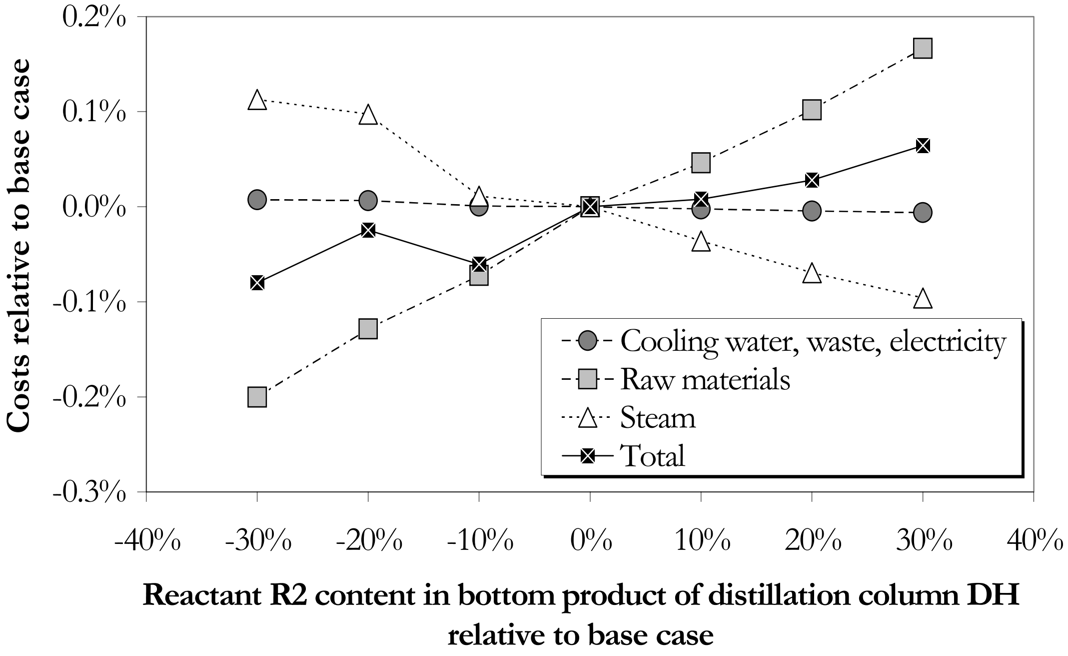


Figure 7-6: Sensitivity analysis of the reactant R2 content in the bottom product of distillation column DH with regard to variable costs

In difference to the previously discussed parameter sensitivities, the resulting total costs only vary by roughly ±0.2%. Additionally, the steam costs which are mainly influenced by the heat requirements of the distillation columns DI and DP do not dominate the total costs in this parameter variation. Instead, the raw material costs are more sensitive than the steam costs while the combined costs for cooling water, waste disposal, and electricity are almost completely insensitive to the reflux ratio. With respect to decreasing R2 contents, the raw material costs decrease whereas the steam costs increase. Since the variation more strongly affects the raw material costs (same explanation as in the last two sections) than the steam costs, the total costs also decrease. Interestingly, the shape of the steam cost curve seems to follow a linear relationship for R2 contents above 1.0 wt% – yet this relationship changes for contents below 1.0 wt%. This strange behaviour might be due to insufficient calculation precision, especially since the cost sensitivities are generally low.

7.4.8 Contents of reactants R1 and R2 in the overheads of distillation column DP (FP6)

The contents of reactants R1 and R2 in the overheads of distillation column DP can be varied by manipulating the column reflux ratio. If the reflux ratio is varied both contents respond in the same direction, e.g. if the reflux ratio is decreased, both contents increase in the overheads and vice versa. In parallel, the product P recovery in the overheads is held constant by varying the column distillate rate. The reflux ratio is varied from +35% to -8% as compared to its inital value, which in turn causes the content of reactant R1 to roughly vary from -60% to +70% and the content of reactant R2 to approximately vary from -6% to +5%, both relative to their base case values. The cost sensitivity results are displayed in function of the R1 overhead content in Figure 7-7 and in function of the R2 overhead content in Figure 7-8. The total costs vary from -0.2% to +4.7% of the total base case costs, which indicates a high sensitivity of the investigated optimization parameter. The shapes of the cost curves shown in both figures are similar.

As previously discussed in Section 6.5.3, an azeotrope sets a boundary to the distillation task (purity of product P >95% not feasible). Therefore, the reflux ratio needs to be increased dramatically if the contents of both reactants (R1, R2) in the column overheads is to be reduced. This process behaviour can be observed in the total cost curves of Figure 7-7 and Figure 7-8 with regard to decreasing R1 and R2 contents. The total costs are mostly dominated by the

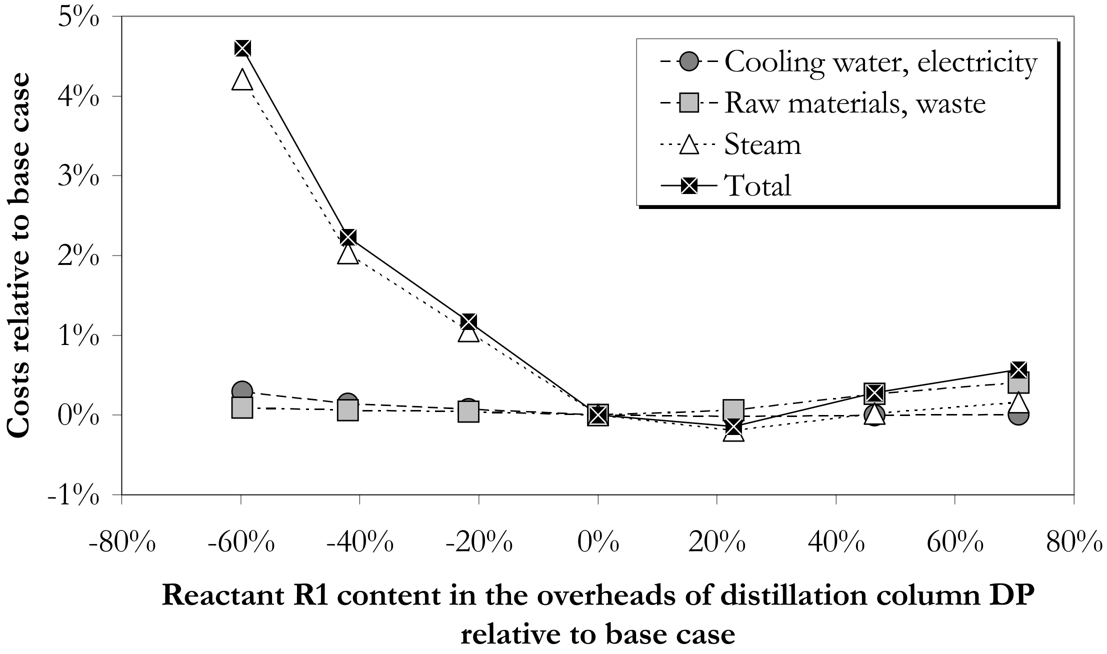


Figure 7-7: Sensitivity analysis of the R1 reactant content in the overheads of distillation column DP with regard to variable costs

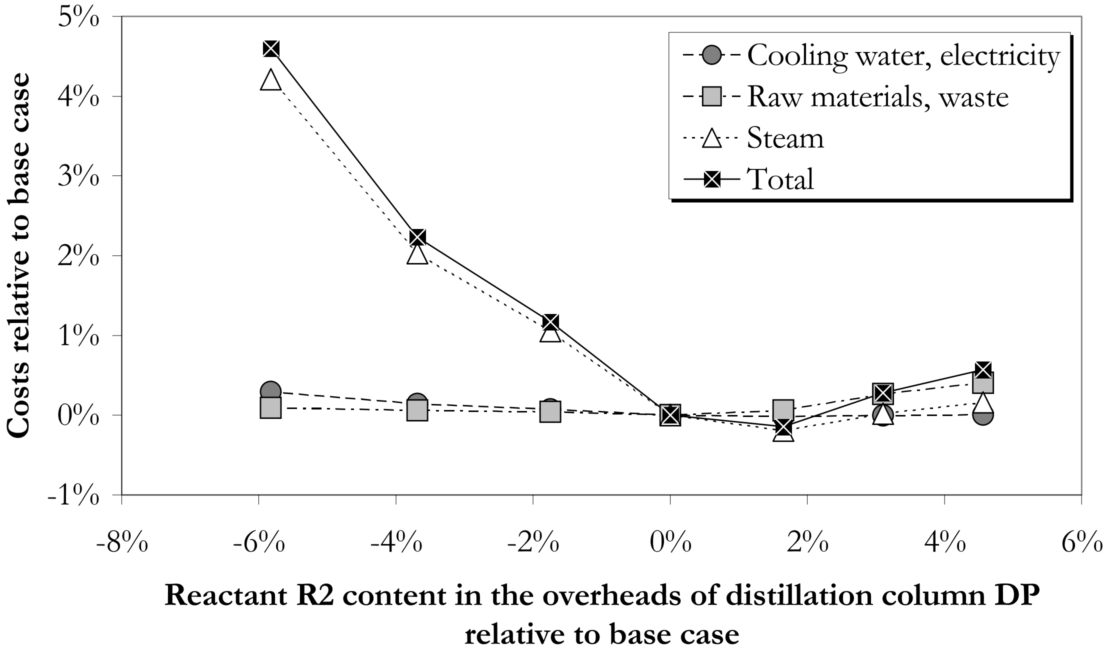


Figure 7-8: Sensitivity analysis of the R2 reactant content in the overheads of distillation column DP with regard to variable costs

steam costs for reactant R1 and R2 contents below the base case contents. However, in the opposite direction the total costs first decrease to a cost minimum of roughly -0.2% as compared to the total base case costs and then increase continuously. At the same time this part of the total cost curve is dominated by the combined cost curve for the raw materials and the waste disposal. In fact, this change results from the higher R1 reactant content (see Figure 7-7). Because reactant R1 has a bad solubility in water, the fresh water flow-rate to extractor EX ($s_{EX,\,ip}$) increases massively in order to separate enough reactant R1 to fulfill the product quality specifications. The higher fresh water flow-rate in turn increases the steam demand in distillation column DH more than the steam requirements of distillation column DP is lowered due to a lower reflux ratio. This leads to slightly increasing overall steam costs with regard to increasing R2 contents. Apart from that, the cooling water and electricity costs far less sensitive than the steam and raw material costs throughout the range of variation.

7.4.9 Pressure in distillation column DP (FP7)

The pressure in distillation column DP impacts on its separation efficiency. In the base case the absolute column pressure is set to the same value as distillation column DI (2 bar). The pressure is varied by ±15% (1.7 bar to 2.3 bar) as compared to the initial value, which causes the total costs to vary from -4.2% to +5.7% relative to the total base case costs. The resulting costs curves are shown in Figure 7-9.

The total and the steam cost curves exhibit a linear proportionality to the pressure below the base case value. Both curves seem to follow a non-linear proportionality for pressures above 2 bar absolute pressure. The total costs are dominated by the steam costs because the sensitivities of the cooling water, raw material, waste disposal, and electricity costs are weak compared to the sensitivity of the steam costs. The combined cost curve in Figure 7-9 is mostly dominated by the raw material costs in the same manner as described in Sections 7.4.5 and 7.4.6. The column pressure reduction decreases not only the steam consumption in the distillation column DP but also the necessary cooling duties. In analogy to the pressure variation in distillation column DI (Section 7.4.6), the pressure has almost no effect on the energy requirements of other unit-operations.

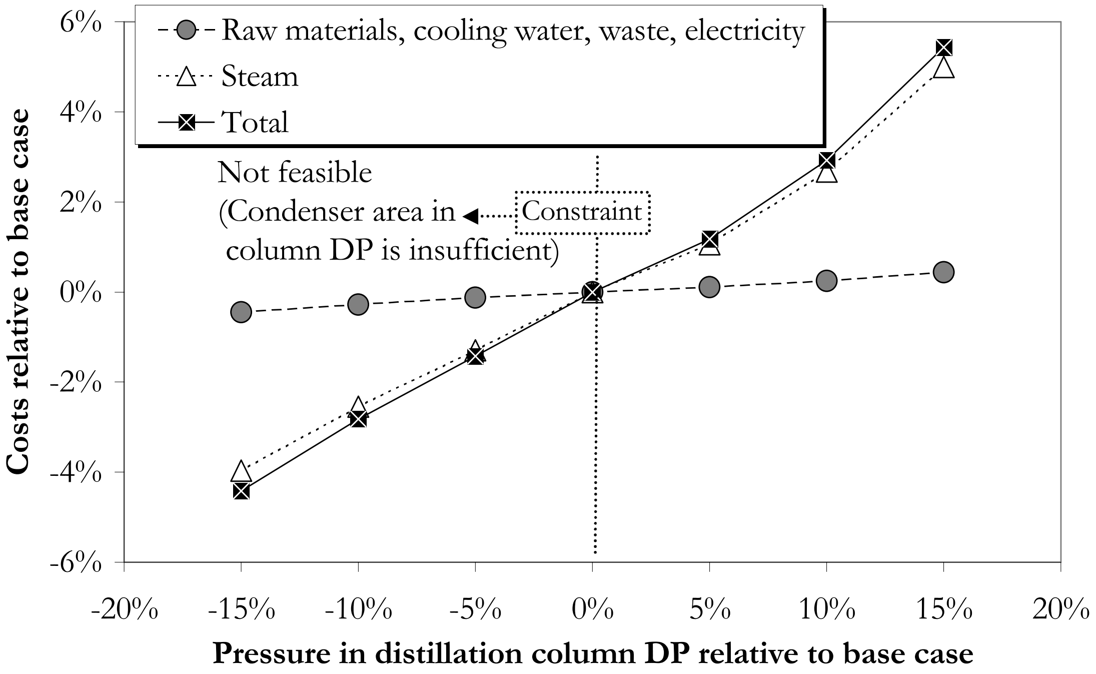


Figure 7-9: Sensitivity analysis of the pressure in distillation column DP with regard to variable costs

7.4.10 Coupled product CP content in the overheads of distillation column DH (FP10)

The separation in distillation column DH yields a low coupled product CP content in the overheads in the base case. This optimization parameter can be controlled by manipulating the column reflux ratio. The reflux ratio itself is varied from +33% to -23% relative to the base case value. This causes the CP coupled product content to vary from -30% to +50% relative to the base case value as displayed in Figure 7-10.

The resulting total costs vary roughly from -0.7% to +0.5% as compared to the total base case costs. Similarly to most of the previously investigated optimization parameters the total costs are dominated by the steam costs. From the shape of the total cost curve in Figure 7-10 no statement can be made about the order of proportionality from the coupled product CP content in the overheads of distillation column DH. The deviations of the calculations from an approximately linear proportionality could be due to insufficient calculation accuracy. In the direction of increasing CP contents the steam savings result only from a reduction of the reflux ratio in distillation column DH.

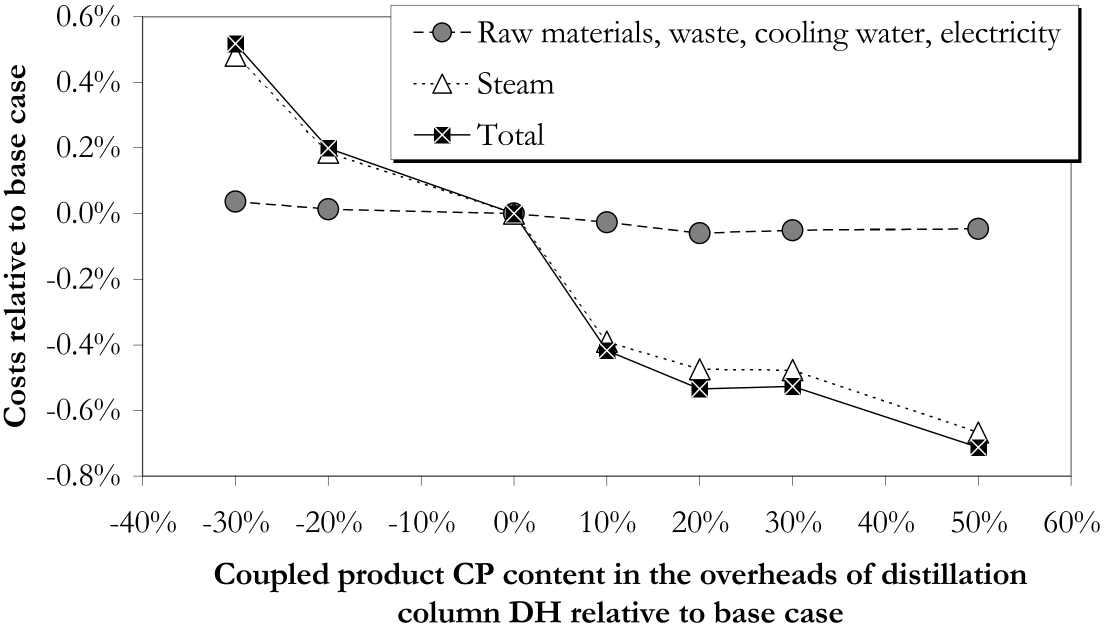


Figure 7-10: Sensitivity analysis of the water content in the overheads of distillation column DH with regard to variable costs

However, at the same time the steam requirements in distillation columns DI and DP increase. In the opposite direction these trends are reversed accordingly. The cost sensitivities of the raw materials, the waste disposal, the electricity, and the cooling water are much less important than the cost sensitivity of the total steam consumption.

7.4.11 Fresh water flow-rate $s_{EX,ip}$ to extractor EX (FP11)

The fresh water flow-rate $s_{EX,\,ip}$ controls the quality specifications of the product flow $d_{EX,\,op}$. Yet, in the investigated base case the component purities of the product flow exceeds the quality specifications by a fair margin so that there is still considerable room to reduce the fresh water flow-rate. The optimization parameter is varied by ±15% of its base case value which yields a total cost variation roughly from -0.5% to +0.3% relative to the total base case costs. The results are displayed in Figure 7-11.

In this sensitivity study the total costs are not completely dominated by the steam costs because the raw material cost curve and the combined cost curve for cooling water, waste, and electricity exhibit cost sensitivities higher than

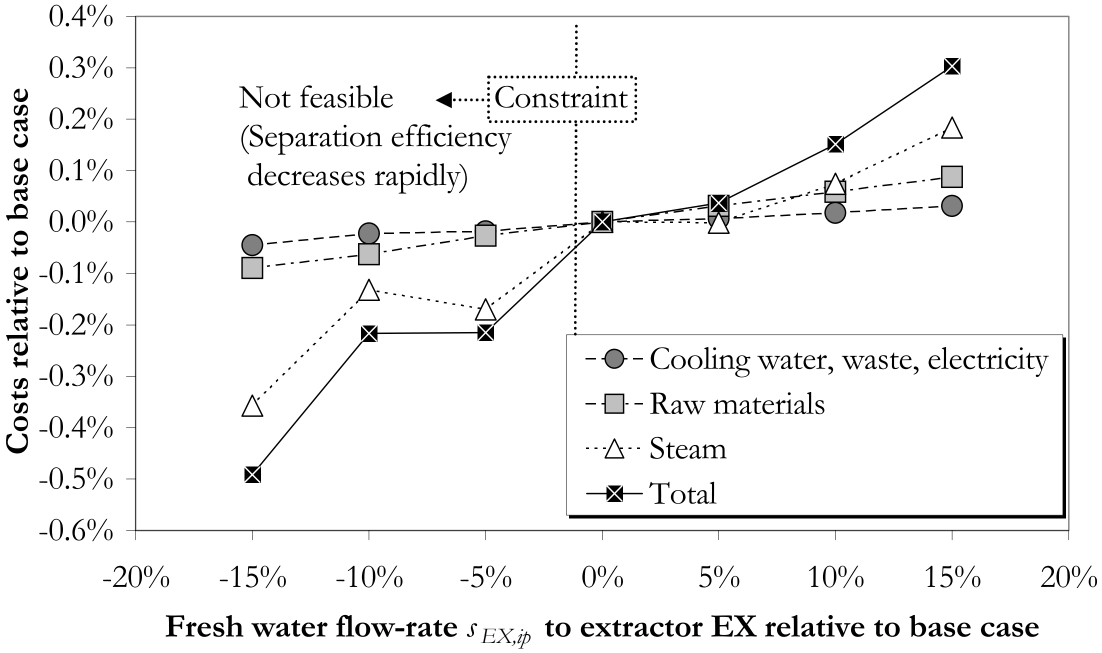


Figure 7-11: Sensitivity analysis of the fresh water flow-rate $s_{EX,ip}$ to extractor EX with regard to variable costs

usual as compared to the steam cost sensitivity. The shape of the steam cost curve however causes the total cost curve to deviate from a linear proportionality to the fresh water flow-rate.

These deviations are probably not due to insufficient calculation accuracy in this case. With regard to decreasing fresh water flow-rates the steam costs for distillation column DI first increase and then suddenly decrease again, whereas the steam requirements of the reboiler in the distillation column DH constantly decrease. The sum of both cost trends yields the observed shape of the total steam cost curve. In the opposite direction the steam costs for distillation column DH increase while the steam costs for distillation column DI decrease. Because of the heat integration described in Section 3.5.1 the steam requirements of all three distillation columns DI, DP, and DH are linked to one another. If the total flow-rate of the overheads is reduced in column DH, less process heat is available in the columns DI and DP and the fresh steam flow-rate necessarily increases. However, in this case a reduction of the water load in column DH only has little effect on its overheads flow-rate (or reflux ratio) because water completely leaves distillation column DH in the bottom product.

The combined cost curve for cooling water, waste, and electricity is especially influenced by the waste disposal costs as more water has to be sent to the waste treatment plant if the fresh water flow-rate $s_{EX,\,ip}$ is increased. For the same reasons the raw material costs also increase because the reactant R2 content is kept constant in the bottom product and therefore more fresh reactant R2 has to be introduced to the process in $s_{MI1,\,ip}$.

7.4.12 Pressure in distillation column DH (FP12)

The pressure in distillation column DH impacts on its separation efficiency. In the base case the absolute column pressure is set to roughly 6.6 bar absolute pressure. The pressure is varied from -40% to +14% of this base case value (4.0 bar to 7.5 bar), which causes the total base case costs to vary within the range of -0.5% to +0.15%. The resulting costs curves are shown in Figure 7-12.

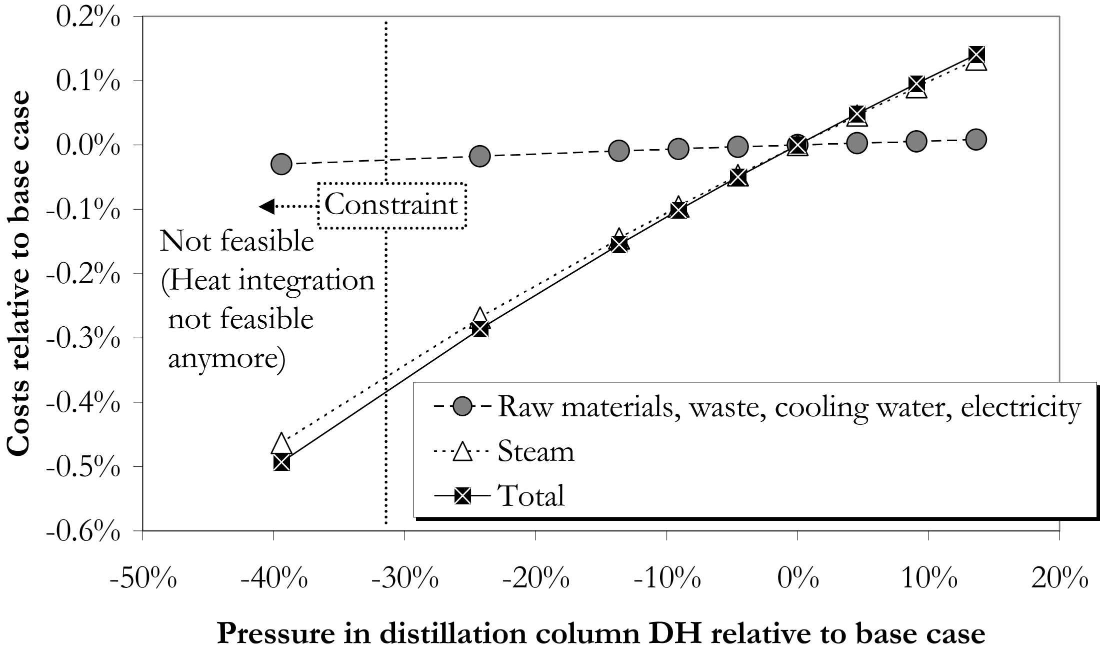


Figure 7-12: Sensitivity analysis of the pressure in distillation column DH with regard to variable costs

The total and the steam cost curves altogether exhibit a fairly low cost sensitivity and approximately linear proportionality to the pressure in the interval over the entire variation range. The total costs are dominated by the steam costs similarly to the reasons previously discussed in Sections 7.4.6 and 7.4.9. The sensitivities of the cooling water, raw material, waste disposal, and electricity costs are weak compared to the sensitivity of the steam costs. The major contributions to the combined cost curve (raw materials, waste, cooling water, and electricity) in Figure 7-12 stem from the cooling and electricity costs. In fact, a reduced column pressure not only decreases the steam consumption in the distillation column DH but also the condensation duties for its overheads that are not used to heat the reboilers of the other distillation columns. Since the DH distillation column condenser is operated with cooling water and air ventilation (electricity) the aforementioned cost sensitivities of cooling water and electricity are to be expected.

In analogy to the pressure variation in distillation columns DI and DP (Sections 7.4.6 and 7.4.9), the pressure has almost no effect on the energy requirements of other unit-operations. However, the previously described heat integration (see Section 3.5.1) between the three distillation columns explains why the cost sensitivity for a pressure variation in column DH is much less than compared to the pressure variation in distillation columns DI and DP.

7.4.13 Interpretation of the sensitivity results

The sensitivity analysis (see Section 7.4) of the identified optimization parameters from Table 6-8 do not include the RK2 reactor temperature and pressure (optimization parameters FP8 and FP9, respectively) because no reaction kinetics are available for the main reaction *(REq. 3-4)* in reactor RK2. The sensitivity analysis shows that the most important cost sensitivities essentially result from changing steam requirements in the reboilers of the three distillation columns DI, DH, and DP. In almost all parameter variations the raw material, waste, electricity, and cooling cost sensitivities are far below the steam cost sensitivities. The following Table 7-1 shows the type of proportionality of the total costs to the varied optimization parameter, the base case values of

Table 7-1: Sensitvity results of the identified optimization parameters of the Fine Chemical case study

Optimization parameters varied in the sensitivity analysis	Total cost proportionality[a]	Constraint[b]
FP1 – Reactor RK1 outlet temperature	linear	<-0.2%
FP2 – Reactant R1/R2 feed mass-ratio to reactor RK1	non-linear (cost minimum inside interval)	-
FP3 – Reactant R2 recovery in the overheads of distillation column DI	non-linear (cost minimum inside interval)	-
FP4 – Pressure in distillation column DI	linear	<-15%
FP5 – Reactant R2 content in the bottom product of distillation column DH	approx. linear	-
FP6 – Contents of reactants R1 and R2 in the overheads of distillation column DP	non-linear (cost minimum inside interval)	-
FP7 – Pressure in distillation column DP	linear	<0% (cannot be reduced)
FP10 – Coupled product CP content in the overheads of distillation column DH	approx. linear	-
FP11 – Fresh water flow-rate $s_{EX,\,ip}$ to extractor EX	approx. linear	<-2.2%
FP12 – Pressure in distillation column DH	linear	<-32%

a. As observed in the investigated interval and discussed in Section 7.4.

b. Known constraints due to equipment capacity limitations or quality requirements in the investigated interval in the direction of decreasing variable costs (relative to the base case values).

each optimization parameter, and the nearest process constraint (equipment capacity or quality requirement) for each optimization parameter as described in Section 7.4.

The optimization parameters FP1, FP4, FP7, and FP8 display a linear proportionality to the total variable costs. Among these, especially the variation of parameters FP1, FP4, and FP7 exhibit important total cost sensitivities and result in cost savings if their respective values are lowered. A variation of the pressure in distillation column DH (FP8) yields a much lower total cost sensitivity as already indicated by its low total cost impact potential (see Table 6-8). Parameter FP1 cannot be lowered below approximately -0.2%, because the cooling system itself operates near its minimum cooling temperature. Parameter FP4 can only be lowered to a pressure minimum of approximately 1.7 bar

(-15% relative to the base case value) since below that pressure the desired production-rate of product P cannot be met anymore (lower pressure decreases the residence time in reactor RK2 and the conversion of product P accordingly). Parameter FP7 is constrained by the condensation of the overheads in distillation column DP so that the operating pressure cannot be lowered any further without changing the equipment. Thus this parameter is not included into the parameter optimization. Finally, parameter FP12 can be lowered to a minimum pressure of approximately 4.5 bar. Below this pressure the heat integration between the overheads of distillation column DH and the reboilers of the remaining distillation columns DI and DP cannot be maintained anymore. Parameters FP1, FP4, and FP12 are included into the parameter optimization in the following manner:

- Parameter FP1 is varied by manipulating the coolant flow-rate to reactor RK1 to yield the lowest possible outlet temperature.
- Parameter FP4 is not varied in the optimization but directly set to the lowest possible pressure.
- Parameter FP12 is not varied either in the optimization but directly set to the lowest possible pressure.

The optimization parameters FP2, FP3, and FP6 exhibit a strongly non-linear proportionality to the total variable costs (see Table 7-1) and a cost minimum inside their variation ranges. All three parameters display important cost sensitivities in both directions from their cost minima. No equipment capacity or quality specification constraints are known or expected inside their investigated ranges. The three parameters are therefore included into the parameter optimization and manipulated by the fresh R2 reactant feed-rate in supply flow $s_{MI1,\,ip}$ (FP2) as well as the reflux ratios in distillation columns DI (FP3) and DP (FP6).

Finally, parameters FP5, FP10, and FP11 display an approximately linear proportionality to the total variable costs. However, the cost sensitivities of the last three parameters are generally low. The total costs of the investigated process decrease if parameters FP5 and FP10 are increased, while parameter FP11 needs to be decreased. Parameter FP11, the fresh water feed-rate to the extractor EX in supply flow $s_{EX,\,ip}$ (see Figure 3-6), cannot be decreased by more than 2.2% because otherwise the liquid load in distillation column DH starts to be too low and causes separation difficulties (the column was initially conceived for a much higher liquid load as compared to the base case). The three parameters are handled in the parameter optimization in the following manner:

- Parameter FP5 is not varied in the parameter optimization because of its low cost sensitivity.
- Parameter FP10 is varied by manipulating the reflux ratio in distillation column DH.
- Parameter FP11 is not varied but set to a slightly higher flow-rate (+9% as compared to the base case value) in order to ensure the desired separation efficiency in distillation column DH

It can be concluded that only five optimization parameters – FP1, FP2, FP3, FP5, and FP6 – out of the ten parameters studied in the sensitivity analysis are varied simultaneously in the following parameter optimization. The parameters FP5 and FP7 are not included into the optimization, while the remaining parameters FP4, FP11, and FP12 are directly set to their optimal values as of the results of the sensitvity study.

7.5 Parameter optimization

7.5.1 Description of the optimization model and implementation

The parameter optimization is performed with the more complex optimization model that corresponds to the base case model and thus takes the external feed of the impurity-groups IG1 and IG2 (simulated by two place-holder components) through supply flow $s_{MI2,\,ip}$ and their generation in reactions *(REq. 3-6)*, *(REq. 3-8)*, and *(REq. 3-9)* into account. The optimization model also includes the design specification to keep the desired product P production rate constant, similar to the sensitivity model described in Section 7.4. The SQP-algorithm (Successive Quadratic Programming) that is integrated in Aspen Plus® is chosen for the parameter optimization.

As for the sensitivity analysis (see Section 7.4) the variable process costs are used as objective function. The variation range of the manipulated parameters in the parameter optimization is fixed according to the results of the local sensitivity analysis. The base case values of the manipulated parameters are used to initialize the optimization. A number of optimization runs is then performed with modified initialization values in order to increase the chances of finding the minimum variable process costs.

7.5.2 Results of the parameter optimization

The optimized values of the considered parameters are compared to their base case values in Table 7-2. If an optimization parameter is indirectly varied by manipulation through another process parameter the table also shows the base case and optimized values.

As expected the optimized value for the RK1 reactor outlet temperature (FP1) is equal to the minimum possible outlet temperature (-0.2% – see Table 7-1). Surprisingly, the cooling duty in the cooling system drops by 6%, although the outlet temperature actually decreases. This occurs because the total flow-rate at the entrance of reactor RK1 decreases as a result from other parameter changes and therefore less cooling duty is needed to reach the minimum cooling temperature difference (see previous section). The reactant feed mass-ratio to reactor RK1 (FP2) increases by roughly 25%, which massively reduces the excess of reactant R2 at the reactor entrance by reducing the fresh R2 reactant feed-rate $s_{MI1,\,ip}$ by 16%. The R2 reactant recovery in the overheads of the distillation column DI is decreased by 5%, which is achieved by increasing the column mass reflux ratio by 16%. Considering the findings from the sensitivity study for parameter FP6 (contents of reactants R1 and R2 in the overheads of distillation column DP – see Figure 7-7 and Figure 7-8) the optimized values first seem surprising because they are further away from

Table 7-2: Base case and optimized values of the selected optimization parameters of the Fine Chemical case study

Optimization parameters from Table 6-8[ab]		Comment	Optimized values[b]
FP1 –	Reactor RK1 outlet temperature [cooling duty]	varied	-0.2% [-6%]
FP2 –	Reactant R1/R2 feed mass-ratio to reactor RK1 [fresh water feed-rate $s_{EX,\,ip}$ to extractor EX]	varied	+25% [-16%]
FP3 –	Reactant R2 recovery in the overheads of distillation column DI [mass reflux ratio of column DI]	varied	-5% [+16%]
FP4 –	Pressure in distillation column DI	new value fixed	-15%
FP6 –	Contents of reactants R1 and R2 in the overheads of distillation column DP [mass reflux ratio of column DP]	varied	-13% R1, -8% R2 [+3%]
FP10 –	Water content in the overheads of distillation column DH [mass reflux ratio of column DH]	varied	+50% [-21%]
FP11 –	Fresh water flow-rate $s_{EX,\,ip}$ to the extractor EX	new value fixed	+9%
FP12 –	Pressure in distillation column DH	new value fixed	-32%

a. The abbreviations for the components in the Fine Chemical process refer to Section 3.5.1 and Figure 3-6.

b. The deviations are shown relative to the base case values.If a selected optimization parameter is indirectly manipulated by another process parameter, the latter appears in brackets.

the calculated cost optimimum than the base case values. Yet, the column mass reflux ratio itself is only minimally increased by 3%. In fact, since the excess amount of reactant R2 is decreased at the entrance of reactor RK1 (by an increased parameter FP2) the product P/reactant R2 ratio in the feed of distillation column DP automatically increases. The new product P, reactant R1, and reactant R2 concentrations in the feed of this column result in a shift of the cost optimum contents of reactant R1 and R2 in the overheads to the left in Figure 7-7 and Figure 7-8. Finally, the water content in distillation column DH is increased by 50% (the R2 reactant content in the bottom is kept constant at its base case value) by lowering the reflux ratio 21%. This result is again expected from the findings of the sensitivity study in Figure 7-10.

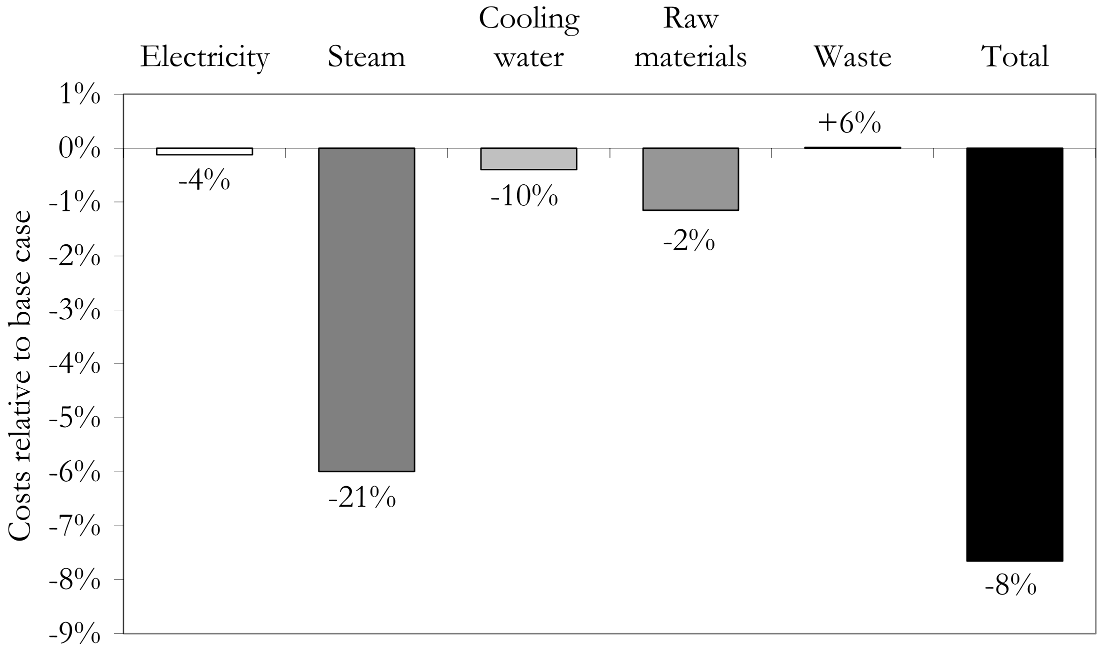


Figure 7-13: Differences in the different variable process cost categories as compared to the base case

The cost differences between the optimized Fine Chemical process and its base case are shown in Figure 7-13 for the variable cost categories electricity, steam, cooling water, raw materials, and waste. The total costs are decreased by -8% as compared to the base case. As observed in the sensitivity analysis the reduction of the steam costs by 21% in the steam category is the most important contribution to the total variable cost savings with approximately 78%. The raw material cost savings represent the second most important cost contribution with 15% of the total variable cost savings although the raw material costs only decrease by approximately 2% in the raw material category. Further, the cooling water and the electricity cost savings together have a minor effect on the total cost savings with roughly 5% (-10% in the cooling water category) and 1.6% (-4% in the electricity category), respectively. The increase in waste disposal costs of +6% in the waste cost category results from the higher bottom product flow-rate from distillation column DH (higher fresh water feedrate to extractor EX – optimization parameter FP11 in Table 7-2) but only slightly affects the total costs.

Table 7-3: Most important changes in energy duties of unit-operations

Most important unit-operations	Utility	Relative change[a]
Reboiler duty of distillation column DH	Steam	-35%
Cooling duty of reactor RK2	Cooling water	-16%
Reboiler duty of distillation column DI	Steam	-8%
Cooling duty of distillation column DI	Cooling water	-7%
Cooling duty of reactor RK1	Electricity	-6%
Reboiler duty of distillation column DP	Steam	+3%

a. Energy consumption relative to the base case values.

The most important cost savings contributions per unit-operation are listed in Table 7-3. The reboiler duties of the distillation columns DH and DI are reduced by roughly 35% and 8% which mostly result from the changes in parameter FP2, FP3, and FP10. For the same reason the cooling duties for reactor RK2, distillation column DI, and reactor RK1 drop by 16%, 7%, and 6%, respectively. In the optimum the reboiler duty of distillation column DP increases only slightly by 3% as compared to the base case.

7.6 Additional structural retrofit alternatives

The total cost sensitivities of the pressure variations in distillation columns DI and DP (optimization parameters FP4 and FP7 in Table 7-1) are among the most important from the results of the sensitivity analysis. Both distillation columns operate in the base case at 2.0 bar absolute pressure and exhibit considerable cost savings if the pressure in the columns could be lowered. Ideally, the column pressures should be reduced to atmospheric pressure even though process constraints prevent the pressure of column DI to be further lowered than 1.7 bar and the pressure of column DP to be lowered at all. In principle the overheads of both columns could still be condensed with the normal cooling water because both overhead temperatures exceed 40°C at atmospheric pressure.

As previously described in Section 7.5.2 at pressures below 1.7 bar in column DI the residence time in reactor RK2 (gas phase reaction) is no longer sufficient in order to guarantee the same conversion as in the base case. Therefore, a structural retrofit alternative could be conceived to repressurize the atmospheric overheads of column DI to approximately 2.0 bars. Unfortunately the overheads are not condensed so that a conventional pump cannot be used. Thus, the best available option would consist in a gas compressor to repressurize the column vapor overheads. However, considering that compressors generally consume considerable amounts of electrical power and cause a good deal of investment costs this structural retrofit alternative is analyzed in more detail in the next chapter. The new structural retrofit alternative is referred to in the following as *alternative FS8*.

On the other hand, the pressure in distillation column DP cannot be decreased because the heat exchange area of the column condenser is too small to completely condense the overheads if the overhead temperatures decrease in response. In this case the obvious structural retrofit alternative would be either to replace the column condenser with an appropriate one or to add a new condenser to the column. In fact, due to rather low investment costs for heat exchangers in general, this structural retrofit alternative seems quite promising. This alternative is therefore also investigated in more detail in the next chapter and is referred to as *alternative FS9*.

7.7 Discussion and conclusions

The results of the parameter optimization show that the base case costs for the Fine Chemical process could be ideally reduced by approximately 8%. Of course, process plants never operate at a constant steady state but are subject to dynamic variation for manifold reasons (e.g. external disturbances, varying feedstocks, process control measures). Therefore the cost savings are subject to these variations as well.

7.7.1 Prediction accuracy of the sensitivity and optimization models

Although the base case model represents the investigated process with reasonable accuracy, an important topic to discuss is the prediction accuracy of the sensitivity and optimization models within Aspen Plus®. The accuracy depends upon multiple aspects:

a) The accuracy of the kinetic data for the main reaction *(REq. 3-3)* in reactor RK1 (Figure 3-6) and the lack of kinetic data for the main reaction *(REq. 3-4)* in reactor RK2.

b) The accuracy of the pure component data, the binary component data on vapor-liquid-equilibria (VLE) and liquid-liquid-equilibria (LLE), the extrapolation on multi-component mixtures, and the applied property method.

c) The model simplification to take the impurity components into account with the help of two place-holder components that represent the two impurity-groups IG1 and IG2.

d) The quality of the unit-operation models selected for the optimization model (e.g. degree of detail, model equations).

e) The error tolerance for all flash-calculations and for the termination of the iterative flowsheet calculations due to the recycles present.

a): The kinetic model for the main reaction in reactor RK1 is not based on the actual reaction mechanism itself. In fact, the reaction orders are assumed and the kinetic parameters fitted to experimental results. Therefore, any extrapolation of the kinetic model onto temperatures and reactant ratios (reactant R1/ R2 ratio) that are not within the range of experiments are potentially dangerous. The kinetic model is actually extrapolated to reactant R1/R2 feed mass-ratios slightly outside the range of experiments. Yet, the sensitivity and optimization results do not seem to contradict the process knowledge gathered. Unfortunately, no kinetic data is available for the main reaction in reactor RK2. This lack of information restricts the representation to a simple black-box RSTOIC-model with constant conversions. Although the conversion in reactor RK2 is known to be reasonably constant during normal plant operations no statements with regard to prediction accuracy can be made on the assumption of a constant conversion in the reactor model.

b) and c): Most of the important pure and binary component data for the intermediate product I, coupled product CP, and final product P were measured. The data on the R1 and R2 reactants were directly retrieved from literature as well as from the internal Aspen Plus® databanks. It is assumed that the pure and binary component data are sufficiently accurate to reasonably predict the process behaviour for the main components (reactant R1, reactant R2, intermediate product I, coupled product CP, product P, water) even in multicomponent mixtures. Although this data is also believed to be accurate enough for the place-holder components for impurity-groups IG1 and IG2 as well as by-product B it cannot be stated what degree of accuracy this model simplification achieves in the sensitivity and optimization models.

d): The unit-operation models that are used to represent distillation columns DI, DH, and DP, extractor EX, and reactor RK1 are all rigorous models (see Section 3.5.2 and Figure 3-6). The heat exchangers of the process (see more detailed process flowsheet in Figure 3-5) are also modelled with a rigorous heat exchange model, whereas only the heaters and coolers are modelled with the simple HEATER-model. Therefore, the process representation offers a good degree of accuracy. However, since reactor RK1 is a plug flow reactor the representation as a CSTR-model with an appropriate residence-time represents a model simplification. Still, the thermodynamic equilibrium in the main reaction *(REq. 3-3)* is reached at the end of the plug flow reactor and therefore justifies this simplification.

e): The error tolerance for the termination of the iterative tear calculations due to the recycles present in the flowsheet corresponds to the default error tolerance of Aspen Plus®. The overall error tolerance for the flash calculations is chosen to be even much tighter than the default tolerance. Thus, the accuracy of the recycle stream calculations should be adequate enough.

Only one set of mass and energy balances available to which the base case model is fitted is available. It would be necessary to set up mass and energy balances for different process steady-states in order to quantify the prediction accuracy. Unfortunately, this is a very tedious and time-consuming procedure and has not been undertaken. If the prediction accuracy was then discovered not to be adequate enough, more experiments on a lab scale, benchscale, or pilot scale would have to be carried out.

7.7.2 Local or global cost optimum?

Another important topic to discuss is the type of cost optimum that results from the parameter optimization. Generally in the case of a multi-parameter optimization it is almost impossible to prove that a global optimum has been reached. However, in the present case it can be stated that the optimized process represents a local cost optimum and not a global one. In fact, the cost optimum is calculated only by manipulating those parameter optimization that are identified in the generation phase (**Step 5**) of the screening method (optimization parameters for the Fine Chemical process are generated in Section 6.5). As there are of course more parameters that could change even minimally in a parameter optimization the optimized process can only represent a local cost optimum.

8 EVALUATION OF STRUCTURAL RETROFIT ALTERNATIVES: FINE CHEMICAL CASE STUDY

8.1 Description of the evaluation procedure

In this chapter the last step of the screening method is presented (**Step 7** – see Figure 2-3). The structural retrofit alternatives that were generated in **Step 5** (Chapter 6) and in **Step 6** (Chapter 7) are evaluated in more detail. The evaluation approach for the generated structural retrofit alternatives is organized in two levels and the decision structure highlighted in Figure 8-1.

In the following, the evaluation procedure for structural retrofit alternatives is described directly with the evaluation of the generated alternatives for the Fine Chemical case study.

8.1.1 Calculation of attainable cost savings (Level 1)

Before a detailed technical implementation and feasibility study are carried out for each structural retrofit alternative, the attainable cost savings are first calculated in a sensitivity analysis by means of a rigorous process simulation. The cost savings are then determined with simulation models that are based on the optimization model previously used in Section 7.5 but that are costumized for each structural retrofit alternative accordingly (later referred to as *structural simulation models*). In analogy to the sensitivity analysis and parameter optimization in Chapter 7, the flow-rate of product stream $d_{EX,\, op}$ (see process graph in Figure 3-6) remains constant. In the structural simulation models a single problem variable or in some cases a small group of problem variables is manipulated (e.g. reaction conversion, murphree stage efficiencies) while all other problem variables are kept constant. The problem variables mostly consist in process operating parameters and sometimes in equipment design variables. However, these models do not represent detailed technical plant modifications for these alternatives. Instead, a process simulation can be set up in a process flowsheet simulator in a manner that operates outside the range of operations of the investigated process plant (e.g. outside equipment capacity

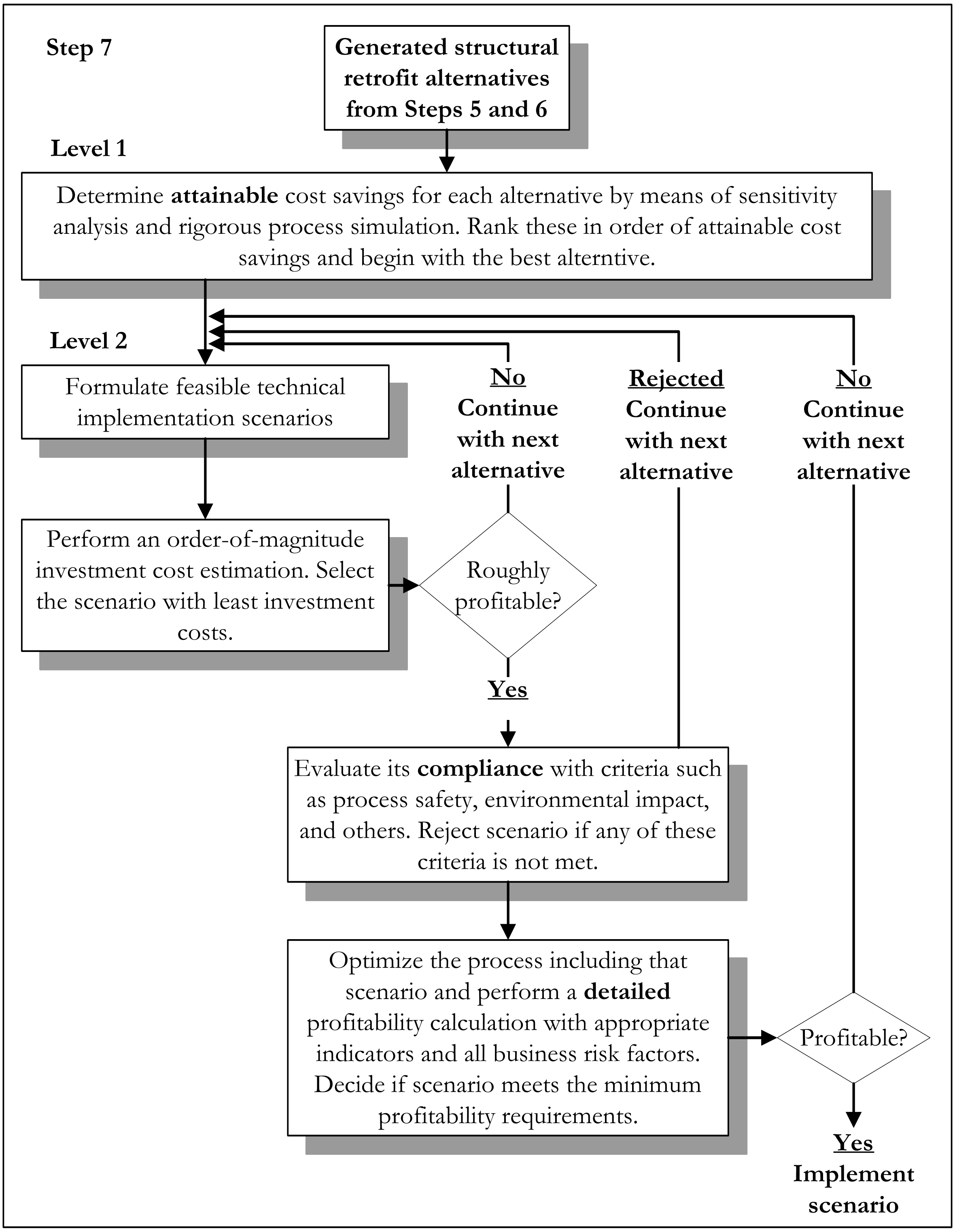


Figure 8-1: Evaluation procedure in Step 7 of the screening method for structural retrofit alternatives (refers to the master scheme of the screening method in Figure 2-3)

constraints, infeasible selectivities for the formation of side-products in a reactor). This entirely depends on the level of detail and the type of models that are used to represent each unit-operation. Further, new unit-operations or altered unit-operations can also be represented as black-box models that perform a desired task (e.g. an idealized separation task) without exact knowledge of the equipment required for the process plant. Still, these simplified simulation models can be used to evaluate different scenarios for each structural retrofit alternative and their attainable cost savings, respectively.

During sensitivity analysis with the structural simulation models it has to be decided in what range the manipulated parameter(s) is (are) to be varied. This range can be limited according to various criteria but has to be independently decided upon for each alternative. On the one hand technical, chemical, and physical limits of the process can restrict the variation range. On the other hand it is only sensible to vary parameters until a maximum in cost savings is encountered.

8.1.2 Selection of the most profitable structural retrofit alternatives (Level 2)

After assessing the cost savings in the described fashion, the structural retrofit alternatives are further analyzed in order of decreasing cost savings (see Figure 8-1). Starting with the alternative that exhibits the highest cost savings feasible solutions for technical implementation (later referred to as *technical implementation scenarios*) are sought. At this stage the decision-maker has to rely on experience and general engineering skills to define suitable technical implementation scenarios. For economic reasons existing and decommissioned equipment should be reused as much as possible to reduce investment costs for new equipment.

In a preliminary investment cost study for each generated scenario (only order-of-magnitude estimation of investment costs) the scenario that incurs the least investment costs is selected. Further evaluation steps should only be undertaken, if this scenario shows potential for economic profitability after a quick calculation e.g. of the Payback Period (*PBP* – see later explanations in Section 8.3.1). Otherwise the next alternative from the list of structural retrofit alternatives has to be investigated.

Any technical implementation scenario that passes this first selection stage then has to satisfy a number of important criteria. In order to comply with those criteria the scenario might have to be slightly modified. Such criteria include:

- Process constraints (e.g. quality specifications, operational constraints) and current equipment capacity limitations have to be taken into account.
- Process safety measures have to be considered.
- Emission limits to the environment have to be met.
- The necessary space for the technical implementation in the process plant, its availability, and its accessability have to be checked.

If the scenario does not comply or cannot be modified to comply with all of these criteria or others that are not mentioned in the list, the scenario should be rejected. Then the next structural retrofit alternative should be selected from the list of structural retrofit alternatives.

A scenario that passes these standards is implemented in a structural simulation model of the investigated process, the variable process costs minimized again and the maximized cost savings determined accordingly. This can be handled in much the same manner as already discussed with the optimization of the Fine Chemical process (Section 7.5). Finally, process operational downtime and eventual production losses during the implementation of that scenario have to be evaluated. Additionally, the costs for installation of new equipment and the costs for eventual de-installation of existing equipment have to be determined. All of this information is finally used to calculate the profitability of the scenario in detail with appropriate economic profitability measures and has to satisfy the company-own minimum profitability criteria including all other business risk factors. If the profitability does not meet the minimum profitability criteria the next alternative from the list of structural retrofit alternatives is investigated. Of course, this evaluation procedure can be continued for all remaining structural retrofit alternatives even when a profitable scenario has already been found.

At first instance, the profitability assessment serves as a decision basis to determine whether a technical implementation scenario is profitable or not. Depending on the chosen profitability criteria (see Section 8.3.1) it can be further used to determine the preference for a particular technical implementation scenario if more than one scenario is profitable.

All together, seven structural retrofit alternatives (alternatives FS1-FS7) were generated in Chapter 6 and two more structural retrofit alternatives (alternatives FS8 and FS9) were generated in Chapter 7 for the Fine Chemical case study. All structural retrofit alternatives are summarized in Table 8-1. The calculation of the attainable cost savings (**Level 1**) of the generated structural retrofit alternatives for the Fine Chemical case study is described in Section 8.2. The variable process cost savings are always calculated relatively to the benchmark of the optimized process from Section 7.5.2 (later referred to as *optimized process*). Finally, technical implementation scenarios are generated and analyzed (**Level 2**) for two examples of structural retrofit alternatives.

Table 8-1: Complete list of the generated structural retrofit alternatives for the Fine Chemical case study

Label[a]	Description of the structural retrofit alternative[b]
FS1	a) Introduce a new reactor type in RK1 to increase the conversion b) Improve the cooling system of reactor RK1 to increase the conversion
FS2	Use better internals in distillation column DH (better separation efficiency)
FS3	Introduce a more selective catalyst for reactor RK2
FS4	Introduce a different separation method to purify product P (instead of extractor EX)
FS5	Introduce a separation method to partially remove IG1 and IG2 from external supply $s_{MI2,\,ip}$
FS6	Introduce a purge in cycle path flow C1 of impurity-group IG1
FS7	a) Introduce a purge in cycle path flow C2 of impurity-group IG2 b) Introduce a more selective catalyst for reactor RK1
FS8	Reduce the pressure in distillation column DI
FS9	Reduce the pressure in distillation column DP

a. Refers to the labels of the structural retrofit alternatives in Table 6-9 and of Section 7.6.

b. The component path flow abbreviations refer to Table 6-6 and the acronyms for the unit-operations refer to the Fine Chemical process graph in Figure 3-6.

8.2 Attainable cost savings of the identified alternatives (Level 1)

8.2.1 Higher conversion in reactor RK1 (FS1)

Both sub-alternatives – (a) the introduction of a new reactor type instead of reactor RK1 and (b) the introduction of a new cooling system for reactor RK1 (see Table 8-1) – aim at increasing the conversion of the first main reaction *(REq. 3-3)* of the process. The cost-savings for the two sub-alternatives are calculated with a structural simulation model almost identical to the optimization model of Section 7.5. In this structural simulation model, reactor RK1 is represented by a CSTR-model in Aspen Plus® (see Section 3.5.2) where the outlet temperature is decreased below the optimized outlet temperature (see parameter optimization results in Section 7.5.2). Although, the refrigeration system in the process plant is not capable of delivering reactor outlet temperatures below the optimized outlet temperature, the CSTR-model directly allows to simulate the effect of a lower outlet temperature on the conversion and the variable process costs. The residence time in the CSTR-model is extended at the same time in order to guarantee that the thermodynamic equilibrium of the first main reaction is reached. As the main reaction conversion is controlled by the temperature (the lower the temperature, the higher the conversion) a temperature variation can be used to determine the cost savings for both sub-alternatives. However, when the conversion increases the reactant R2 recovery in the overheads of distillation column DI (see Figure 3-6) has to be increased to keep the intermediate product I recovery and the coupled product CP content in the distillate constant as calculated in the optimized process. Of course, since no technical implementation scenarios are formulated at this stage, any additional variable utility costs that result from these cannot be taken into account in the cost calculations – i.e. the cooling costs in reactor RK1 from the optimized process are set constant throughout the outlet temperature variation. The results for the two sub-alternatives are shown in function of the outlet temperature and in function of the conversion in Figure 8-2 and Figure 8-3, respectively.

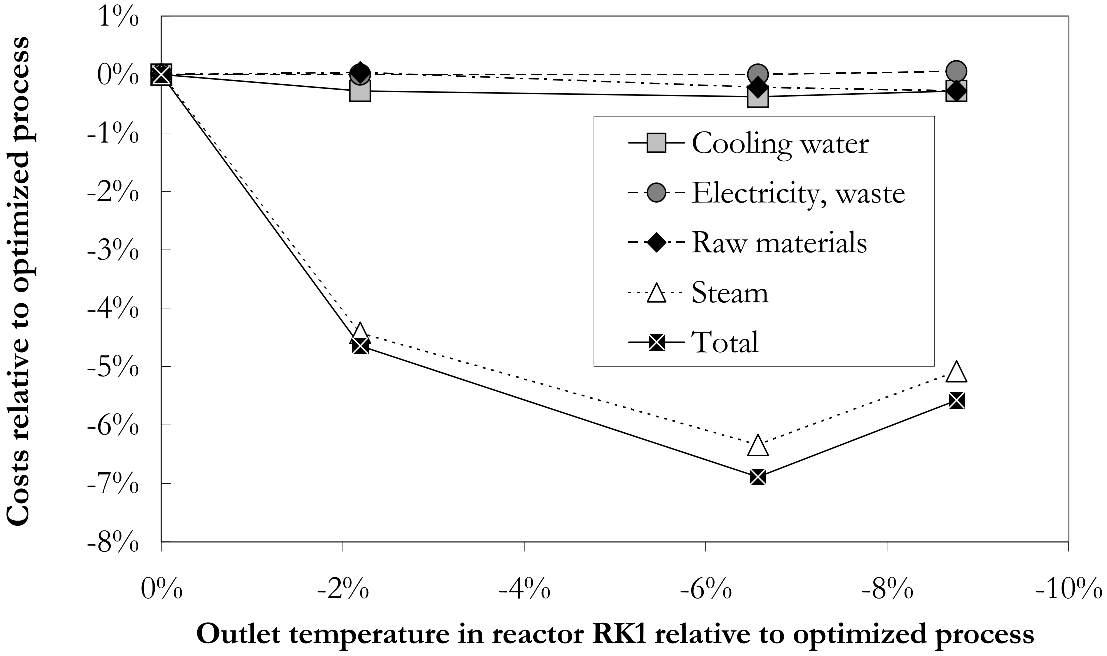


Figure 8-2: Variable process cost savings resulting from decreasing the RK1 reactor outlet temperature relative to the variable costs of the optimized process

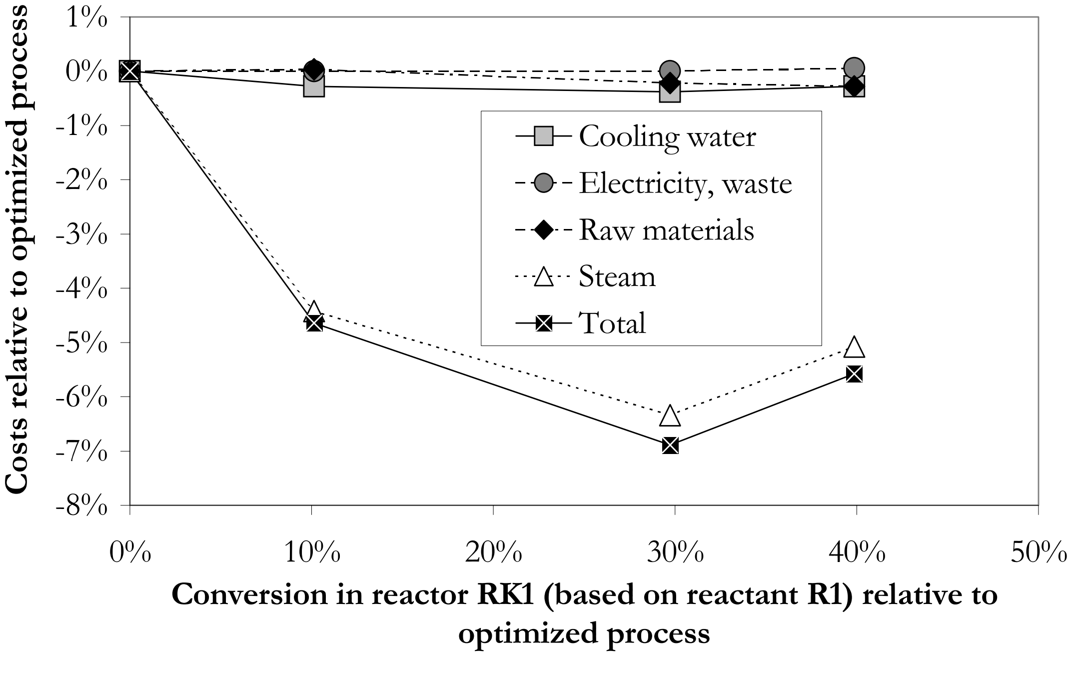


Figure 8-3: Variable process cost savings resulting from increasing the conversion of the main reaction in reactor RK1 relative to the variable costs of the optimized process

In both figures the steam cost curves dominate the total cost curves. The combined curves for electricity and waste disposal costs, the cooling water cost curves, and the raw material cost curves exhibit much lower cost sensitivities as compared to the steam costs. If the temperature is lowered or the conversion is increased the total costs first decrease considerably until they reach a minimum (cost savings of roughly 7% relative to the variable costs of the optimized process). This cost trend change stems from the integration of process heat between the vapor overheads of distillation column DH and the reboilers of the other two distillation columns. If the recovery of reactant R2 in the distillate of column DI is increased, less R2 is fed to column DH and thus less process heat is available for the reboilers of columns DI and DP. Although the reboiling duties of all three columns drop if the conversion increases the heat integration prevents the total costs from a further reduction. It should be noted that a minimum flow-rate of reactant R2 (unconverted and used in excess for the first main reaction) is required in order to achieve a good coupled product CP/intermediate product I separation in distillation column DI. Therefore, the conversion cannot be increased much further than by roughly +40% as compared to the optimized conversion unless the CP/I separation task is solved differently. The variable process cost impact potential of both sub-alternatives suggest that profitable technical implementation scenarios could be found in this case.

8.2.2 Better internals in distillation column DI (FS2)

As the Aspen Plus® RADFRAC-model (simultaneously solves rigorous mass- and energy balances on each stage) is used to represent distillation column DI in the optimization model, it can be directly used to simulate better murphree stage efficiencies. In the optimization model, the component murphree stage efficiencies of reactant R1, reactant R2, intermediate product P, and product P were set to 0.6. The stage efficiencies for the remaining components were adapted to match the recoveries observed in the mass- and energy balances of the base case and were much lower (roughly 0.2). In the following evaluation of alternative FS2, all component murphree stage efficiencies are simultaneously increased step by step by up to +50% of their values in the optimization model. The resulting variable costs are compared to the variable costs of the optimized process and shown in Figure 8-4.

The total costs are again mainly dominated by the steam costs. The cost savings that the combined cost curve for raw materials, waste disposal, electricity, and cooling water exhibits are much lower than compared to the steam cost savings. Higher murphree stage efficiencies especially reduce the reboiler duty in distillation column DH (see Figure 3-6) while the steam requirements of the reboilers in the other two distillation columns DI and DP increase. The combined trend leads to decreasing total costs until a variable costs are reduced by roughly -0.7% at approximately +30% increased separation efficiency as compared to the efficiencies of the optimized process. If the murphree stage efficiencies are further increased, the total costs start to increase again. Because of the rather moderate variable process cost savings of this alternative it is not certain if a substitution of the column internals with more efficient internals could lead to a profitable project.

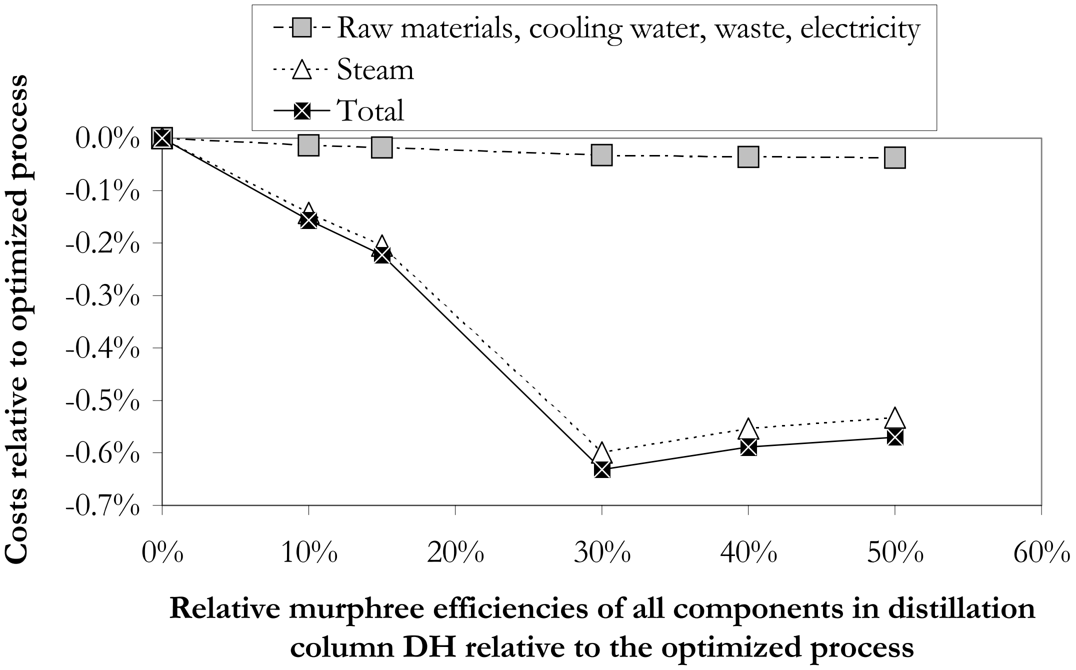


Figure 8-4: Variable process cost savings resulting from increasing the separation efficiency in distillation column DH relative to the variable costs of the optimized process

8.2.3 More selective catalyst in reactor RK2 (FS3)

Beside the second main reaction *(REq. 3-4)*, side-reactions *(REq. 3-7)*, *(REq. 3-8)*, and *(REq. 3-9)* occur simultaneously in reactor RK2 (see Figure 3-6). Alternative FS3 aims at increasing the yield of the main reaction by reducing the formation-rate of by-product B and impurity-group IG1 in these side-reactions. However, if the formation of the impurity-group IG1 in reaction *(REq. 3-8)* is suppressed, a sink for impurity-group IG2 in the process is automatically reduced. Although the *AF*-value of impurity-group IG1 in cycle path flow C1 would be reduced, the *AF*-value of the impurity-group IG2 would be increased as a consequence. Therefore, in this evaluation only the selective reduction of the formation-rate of by-product B in side-reaction *(REq. 3-7)* is analyzed. The optimization model can be used without further modifications to calculate the cost savings of this alternative, because the Aspen Plus® RSTOIC-model is used to represent reactor RK2. In this specific unit-operation model the individual conversions of each reaction can be manipulated, so that the formation-rate of side-reaction *(REq. 3-7)* can be reduced independently. The resulting cost savings are shown in Figure 8-5.

In contrast to the evaluation of the alternatives FS1 and FS2, the raw material costs mainly dominate the total costs in this case. Steam costs, cooling water costs, waste disposal costs, and electricity costs only contribute minimally to the variable cost savings. The total cost curve exhibits an approximately linear relationship to the reduction of the formation-rate of by-product B. In fact, the cost savings in raw material costs are due to reduced reactant R2 losses in the process. Thus, the highest cost savings of roughly 1.5% relative to the total costs of the optimized process are produced at the lowest formation-rate of -60%. This indicates a considerable incentive to reduce the formation-rate of by-product B to the lowest possible level. Therefore, if a more selective catalyst can be found this alternative could be profitable in case its costs do not exceed by far the costs of the catalyst presently used.

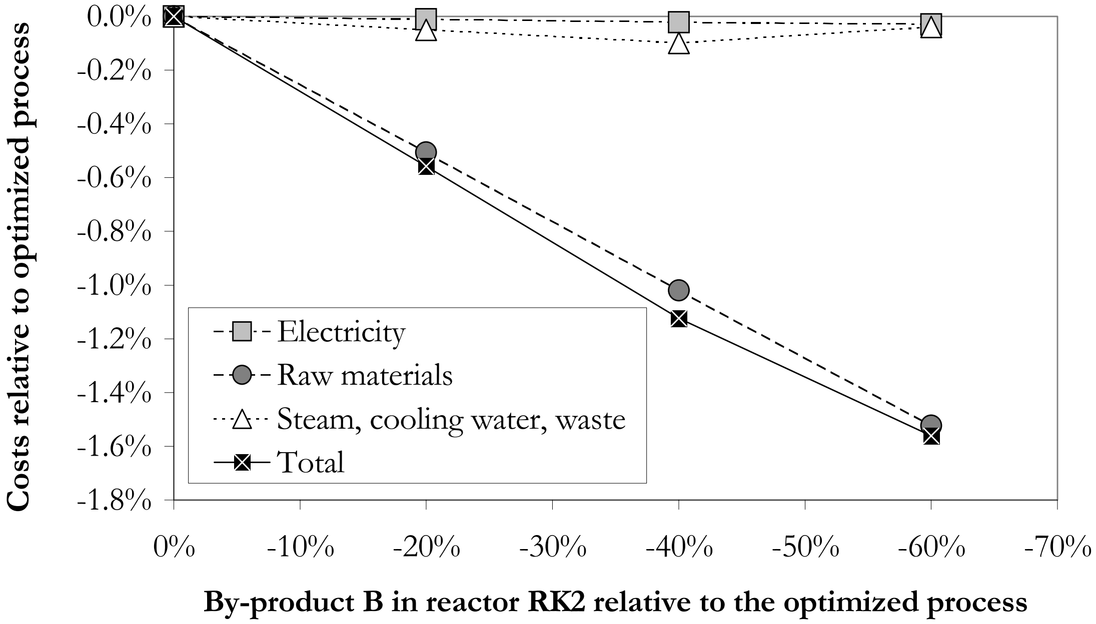


Figure 8-5: Variable process cost savings resulting from a decreasing formation-rate of by-product B in reactor RK2 relative to the variable costs of the optimized process

8.2.4 Different method to purify product P instead of extractor EX (FS4)

Before different separation methods are investigated in order to determine feasible technical implementation scenarios for this alternative, variable process cost savings are evaluated in two scenarios. In Scenario 1 it is assumed that the P product purification is carried out without water as mass separating agent (MSA). It is further assumed that the new separation method yields the same component separations as extractor EX (see Figure 3-6) in the optimized process. In Scenario 2 it is assumed that in addition to Scenario 1 also reactant R1 is completely recycled to the process. In principle, the recycle stream from any such separation method that does not require water as MSA does not have to be fed to distillation column DH to remove water. Instead the recycle stream is directly recycled to the tank in vertex MI1 because it mostly contains reactant R1, reactant R2, and product P. Unfortunately, if no water is fed to distillation column DH from extractor EX the separation efficiency is expected to decrease (column hydraulics). Steam could be directly injected into the bottom stages of the column to provide the required heating duty instead of external reboiling. Thus, the loss of extraction water would be substituted and the column would be able to operate under normal conditions.

The same structural simulation model is used to simulate both scenarios. The main differences to the optimization model consist in using an ideal separation model (SEP-model in Aspen Plus®) to evaluate the two different scenarios, in reconnecting the former EX extractor outlet stream (enriched water stream) with vertex MI1, and to introduce direct steam heating to distillation column DH. In the SEP-model the component separations mentioned above are set for both scenarios and the calculated results shown in Figure 8-6.

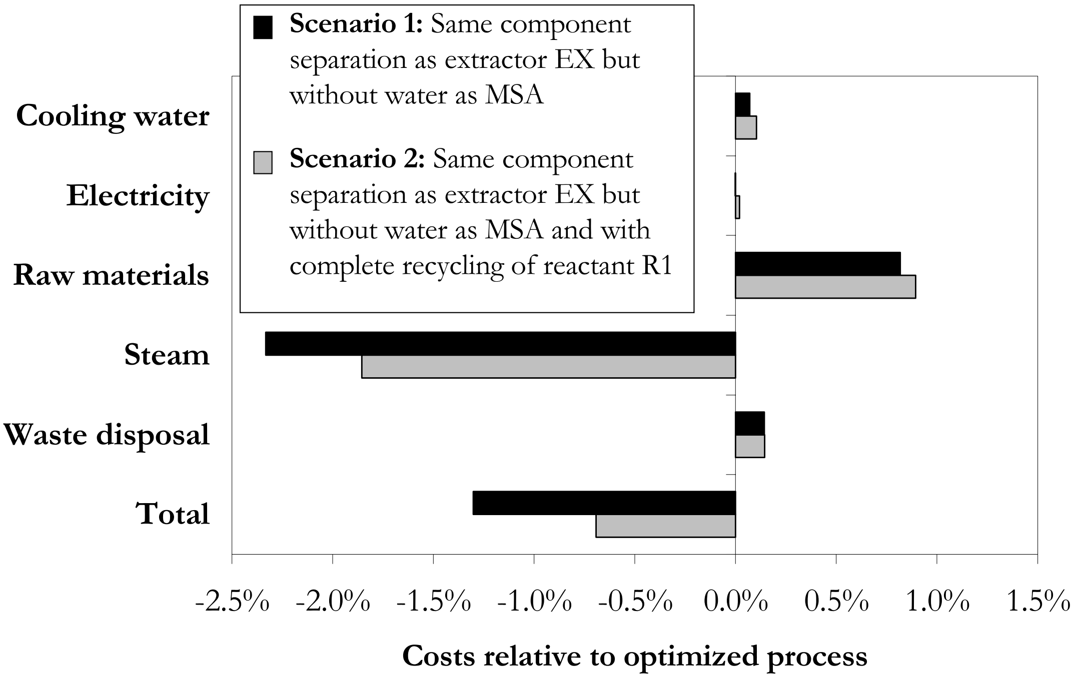


Figure 8-6: Variable process cost savings resulting from two different purification scenarios instead of water extraction in extractor EX relative to the variable costs of the optimized process

It can be seen that in both scenarios costs can only be saved in the steam category. In all other categories the costs increase as compared to the optimized process. Especially the raw material costs and the waste disposal costs increase. The overall steam cost savings for both scenarios stem from a lower (direct) steam requirement in distillation column DH although the other distillation columns DP and DI require more steam than in the optimized process. The direct steam injection into distillation column DH also increases the waste water flow-rate dramatically by +85% of the flow-rate in the optimized process, which leads to higher waste disposal costs in both scenarios. The raw material consumption – mainly of reactant R2 – and accordingly the raw material costs increase because more reactant R2 is lost in the higher waste water flow-rate. Even though reactant R1 is completely recycled in Scenario 2, cost savings with respect to reactant R1 are surprisingly minimal. In the end, the rather moderate variable process cost savings amount to roughly 1.3% in Scenario 1 and to 0.7% in Scenario 2 of the variable costs of the optimized process in both scenarios. Based on these findings and due to considerable investment costs it seems hardly probable that any alternative purification method (e.g. pressure swing distillation) can be expected to be economically profitable.

8.2.5 Separation method to reduce the external supply of impurity-groups (FS5)

The reactions *(REq. 3-6)*, *(REq. 3-8)*, and *(REq. 3-9)* that involve impurity-groups IG1 and IG2 and the external supply of both impurity-groups in $s_{MI2,\,ip}$ (see Figure 3-6) are included in the optimization model previously introduced in Section 7.5. Therefore, this model can be used without further modifications to calculate the variable process cost savings in comparison to the optimized process if the supply flow-rate of both impurity-groups is decreased in $s_{MI2,\,ip}$. The calculation results are presented in Figure 8-7.

The cost curves show that the steam cost savings strongly contribute to the total cost savings. Compared to the evaluation of alternatives FS1-FS3 the raw material costs are much more sensitive in this alternative, while the combined costs for cooling water, electricity, and waste disposal impact the total costs to a lesser degree. The raw material costs increase mainly because the concentration of reactant R1 slightly increases in the final P product stream $d_{EX,\,op}$. A higher make-up reactant R1 feed-rate in $s_{MI1,\,ip}$ has then to be introduced to keep the desired production flow-rate constant in $d_{EX,\,op}$. The steam cost savings stem from reduced steam consumptions in all three distillation columns

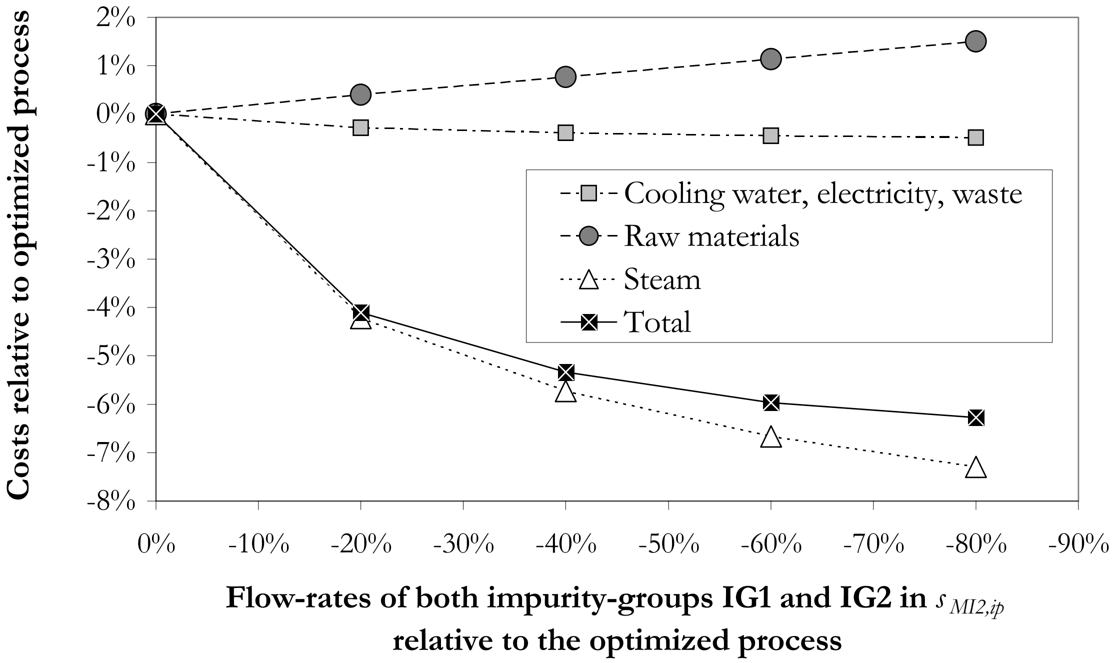


Figure 8-7: Variable process cost savings resulting from decreasing the supply flow-rates of impurity-groups IG1 and IG2 in $s_{MI2,ip}$ relative to the variable costs of the optimized process

DI, DH, and DP. The impurity-groups show a considerable effect on the separation efficiencies in all distillation columns. Therefore, a reduction of the *AF*-values of both impurity-groups in cycle path flows C1 and C2 does not only reduce the steam consumptions because the cycle path flow-rates are decreased. In fact, both effects lead to significant variable process cost savings. The total costs decrease constantly in the investigated variation range to cost savings of roughly 6% relative to the optimized process at -80% of the initial supply flow-rates of both impurity-groups in $s_{MI2,\ ip}$. However, the marginal utility of reducing the two impurity-group supply flow-rates also decreases constantly over the variation range. This indicates that there is little economic sense in completely pre-purifying external supply flow $s_{MI2,\ ip}$ from its impurity-groups. Yet, the variable process cost savings indicate that profitable technical implementation scenarios could be found for this alternative.

8.2.6 Purge in the C1 cycle path flow of impurity-group IG1 (FS6)

The structural simulation model that is used to evaluate this alternative only contains one minor modification to the optimization model of Section 7.5. Since a purge rarely separates only the undesired component(s) from a process, the stream with the highest concentration of impurity-group IG1 has to be determined in cycle path flow C1 beforehand in order to limit the losses of valuable components. The highest concentration of impurity-group IG1 is found on stage 37 (from the column top) in distillation column DP. Therefore, in the optimization model a side-draw that serves as a purge stream is introduced on stage 37 of the unit-operation model that represents distillation column DP (see Figure 3-6). Furthermore, the new structural simulation model does not include any costs or benefits arising from waste treatment of the purge stream (e.g. incineration). The side-draw flow-rates are then increased gradually and the total costs calculated in comparison to the total costs of the optimized process. The evaluation results are shown in Figure 8-8.

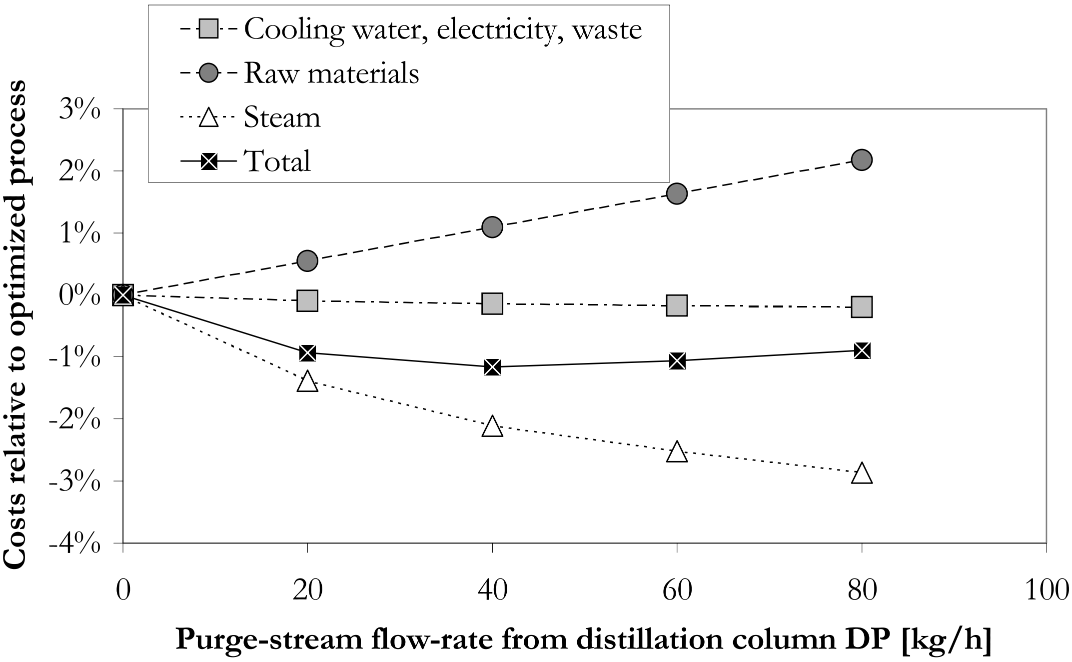


Figure 8-8: Variable process cost savings resulting from different purge-stream flow-rates from distillation column DP relative to the variable costs of the optimized process

Not surprisingly the raw material costs increase almost in linear proportionality to the purge stream flow-rate from distillation column DP since raw materials are directly lost in the purge stream. The combined costs for cooling water, electricity, and waste disposal have a negligible impact on the total costs. On the other hand, the steam costs decrease owing to lower steam requirements in distillation column DI and to a lesser degree in distillation columns DH and DP. This specific behaviour with respect to the steam requirements was already encountered in the previous alternative FS5 (see Section 8.2.5). Yet, as the steam costs do not decrease in linear proportionality to the variation of the purge-stream flow-rate total cost savings of roughly 1.2% as compared to the optimized process can be obtained at a purge-stream flow-rate of 40 kg/h. This indicates that the cost optimum side-draw flow-rate of distillation column DP should be set to roughly 40 kg/h. The profitability of a technical implementation scenario for this alternative is studied in Section 8.3.3.

8.2.7 Purge in the C2 cycle path flow of impurity-group IG2 (FS7a)

This sub-alternative is evaluated in a manner analogous to alternative FS6 and targets a decrease of the IG2 impurity-group accumulation in its cycle path flow C2 similar to alternative FS7b. The structural simulation model that is used to evaluate this first sub-alternative also contains only one minor modification to the optimization model of Section 7.5. The stream with the highest concentration of impurity-group IG2 has to be determined in cycle path flow C2 beforehand in order to limit the losses of other valuable components. The highest concentration of impurity-group IG2 is found on stage 35 (from the column top) in distillation column DH. A side-draw that serves as a purge stream is introduced on stage 35 of the unit-operation model that represents distillation column DH (see Figure 3-6). Moreover, the new structural simulation model does not include any costs or benefits arising from waste treatment of the purge stream (e.g. incineration). The side-draw flow-rates are then increased step by step and the total costs calculated in comparison to the total costs of the optimized process. The evaluation results are shown in Figure 8-9.

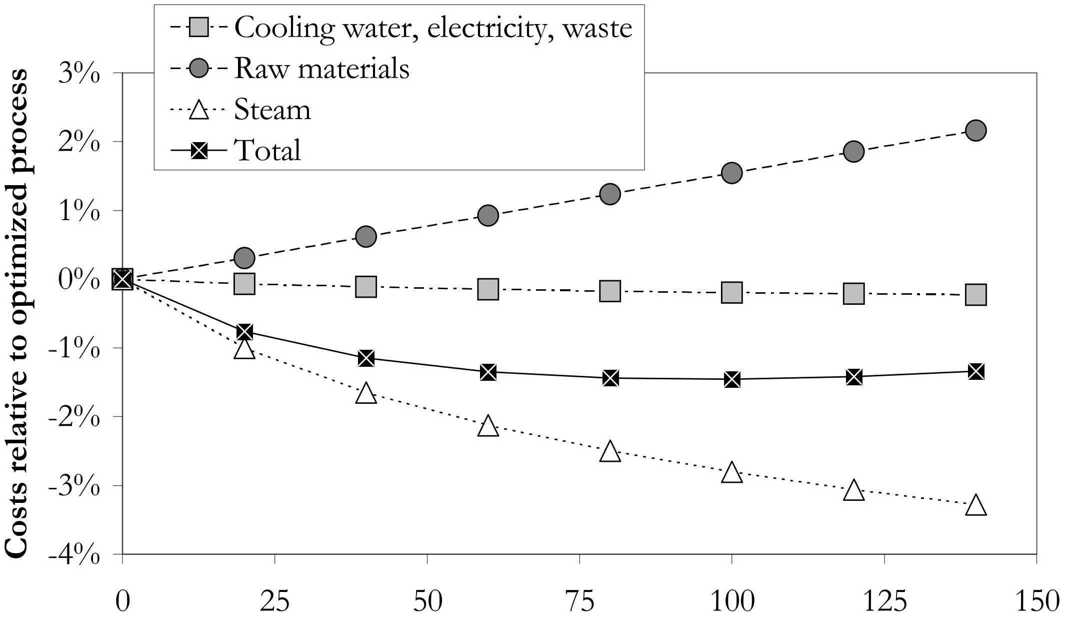


Figure 8-9: Variable process cost savings resulting from different purge-stream flow-rates from distillation column DH relative to the variable costs of the optimized process

As for alternative FS6 in the previous section the raw material costs increase almost in linear proportionality to the purge stream flow-rate from distillation column DH since raw materials are directly lost in the purge stream. The combined costs for cooling water, electricity, and waste disposal have a negligible impact on the total costs. On the other hand, the steam costs decrease because the steam requirements decrease mostly in distillation columns DI and DH, but also to a lesser degree in distillation column DP. Yet, as the steam costs do not decrease in linear proportionality to the variation of the purge-stream flow-rate a total cost minimum of approximately -1.5% relative to the optimized process can be observed at a purge-stream flow-rate of 100 kg/h. Under the assumption that little investment costs are associated with a technical implementation scenario and that no fuel credit is given for energy recuperation by incineration (conservative assumption), this structural retrofit alternative is likely to be profitable.

8.2.8 More selective catalyst in reactor RK1 (FS7b)

This sub-alternative also aims at decreasing the accumulation in the cycle path flow of impurity-group IG2. Besides the first main reaction *(REq. 3-3)*, side-reactions *(REq. 3-5)* and *(REq. 3-6)* occur simultaneously in reactor RK1 (see Figure 3-6). Unlike sub-alternative FS7a this sub-alternative aims at increasing the yield of the main reaction by reducing the formation-rate of impurity-group IG2 in side-reaction *(REq. 3-6)*, which directly reduces its flow-rate in cycle path flow C2. The optimization model can be used without further modifications to calculate the cost savings of this sub-alternative, because the Aspen Plus® RSTOIC-model is used to take the side-reaction *(REq. 3-6)* into account. In this specific unit-operation model the fractional conversion of this side-reaction can be manipulated, so that the formation-rate of side-reaction *(REq. 3-6)* can be reduced. The resulting cost savings are shown in Figure 8-10.

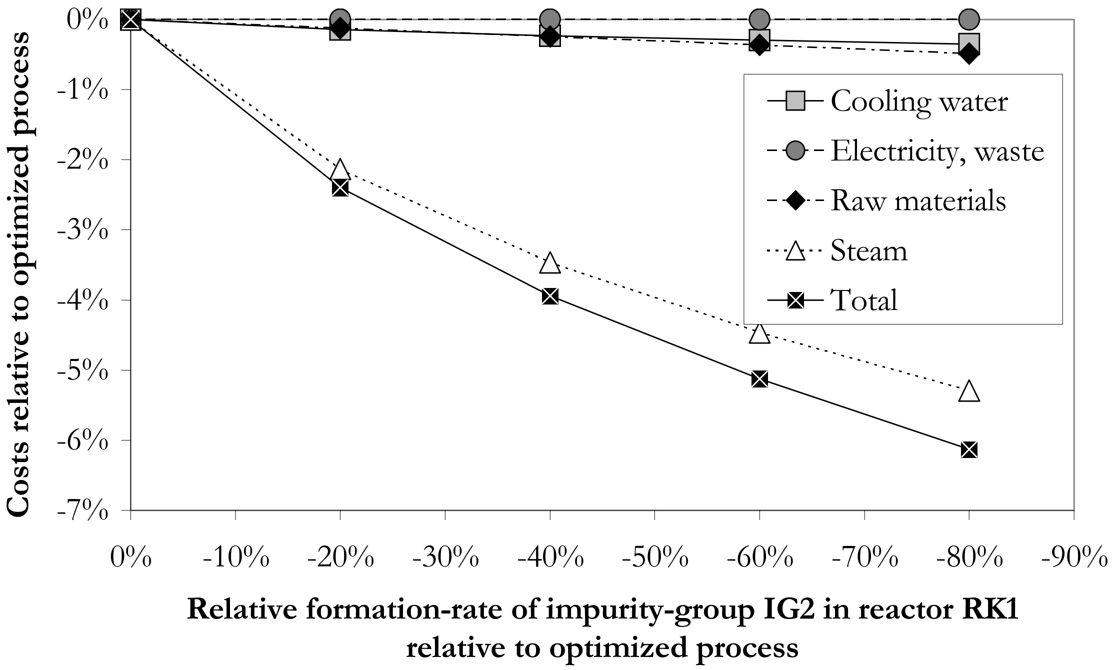


Figure 8-10: Variable process cost savings resulting from a decreasing formation-rate of impurity-group IG2 in reactor RK1 relative to the variable costs of the optimized process

In contrast to alternative FS3 in Section 8.2.3, not the raw material costs but the steam costs mainly dominate the total costs in this case. Raw material costs, cooling water costs, waste disposal costs, and electricity costs only contribute minimally to the variable cost savings. The total cost curve exhibits a strong cost-sensitivity with respect to a decrease of the IG2 impurity-group formation-rate. Yet, as was observed in the evaluation of alternatives FS5 in Section 8.2.5, the sensitivity of the total cost savings decreases itself constantly in the variation range from left to right. The same reasons as described in Section 8.2.5 can be applied to explain this sensitivity behaviour. The highest cost savings of roughly -6% as compared to the variable costs of the optimized process are produced at the lowest formation-rate of -80%. This indicates a considerable incentive to reduce the formation-rate of impurity-group IG2 in reactor RK1 to the lowest possible level. The economic profitability of a new catalyst is highly probable but of course depends on the costs compared to the old catalyst as discussed in Section 8.2.3.

8.2.9 Pressure reduction in distillation column DI (FS8)

The pressure reduction can be directly simulated with the optimization model from Section 7.5 while the pressure in reactor RK2 (see Figure 3-6) is held constant at 2 bar absolute pressure. The pressure of distillation column DI is gradually reduced until atmospheric pressure is reached. Figure 8-11 shows the calculated cost savings.

It can be seen that the steam cost savings represent the most important influence on the total cost savings for alternative FS8. The remaining cost categories (raw materials, cooling water, electricity, waste disposal) have little or no impact on the total cost savings. The total cost curve exhibits an almost linear proportionality to the pressure. As previously commented in the sensitivity analysis on the pressure parameter in distillation column DI (Section 7.4.6) the total cost savings essentially stem from a reduction of the steam and cooling water requirements in the investigated column. At the same time, the costs of all the other unit-operations do not change significantly. If the pressure in distillation column DI can be reduced to atmospheric pressure remarkably high variable process cost savings of roughly -12% relative to the variable costs of

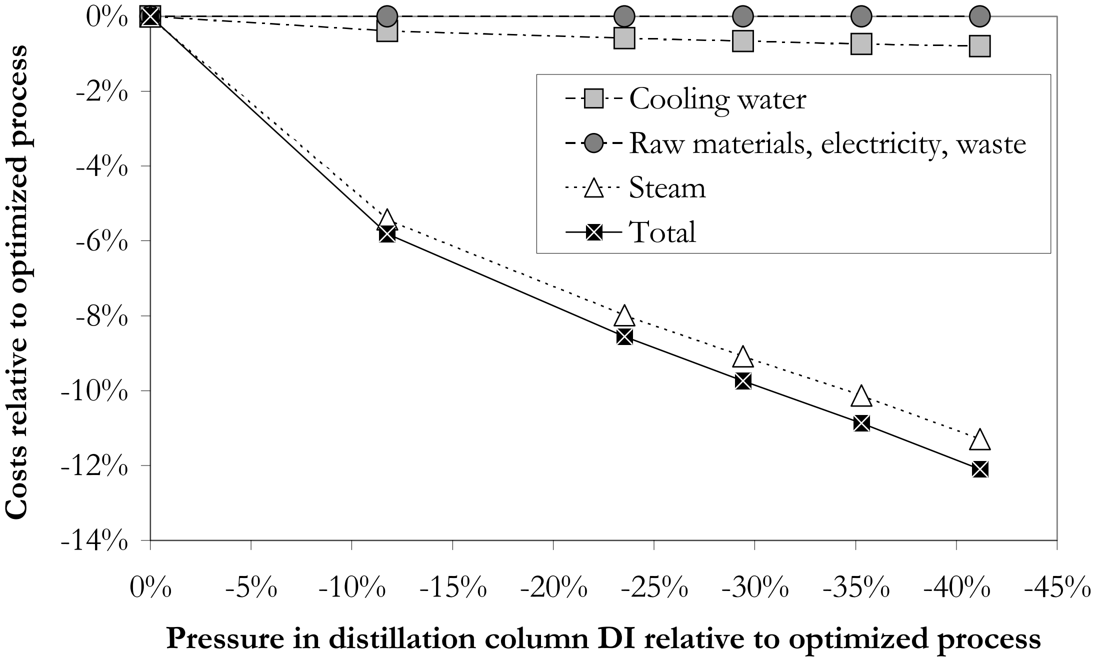


Figure 8-11: Variable process cost savings resulting from a pressure reduction in distillation column DI relative to the variable costs of the optimized process

the optimized process can be achieved. This alternative is investigated in a detailed profitability calculation in Section 8.3.2.

8.2.10 Pressure reduction in distillation column DP (FS9)

This alternative can be directly evaluated with the optimization model from Section 7.5. The pressure of distillation column DP is step by step reduced until a pressure of 1.2 bar (-40%) is reached. The calculated cost savings are presented in Figure 8-12.

Similarly to alternative FS8 in the previous section, the steam cost savings represent the most important influence on the total cost savings. The remaining cost categories (raw materials, cooling water, electricity, waste disposal) have little or no impact on the total cost savings. The total cost curve exhibits an almost linear proportionality to the pressure. Again, the total cost savings essentially stem from a reduction of the steam and cooling water requirements in the investigated column. Below a pressure of 1.6 bar (-20%) the raw material and the waste disposal costs start to increase because more fresh extraction water ($s_{EX,\, ip}$) is required to fulfil the quality specifications with respect to

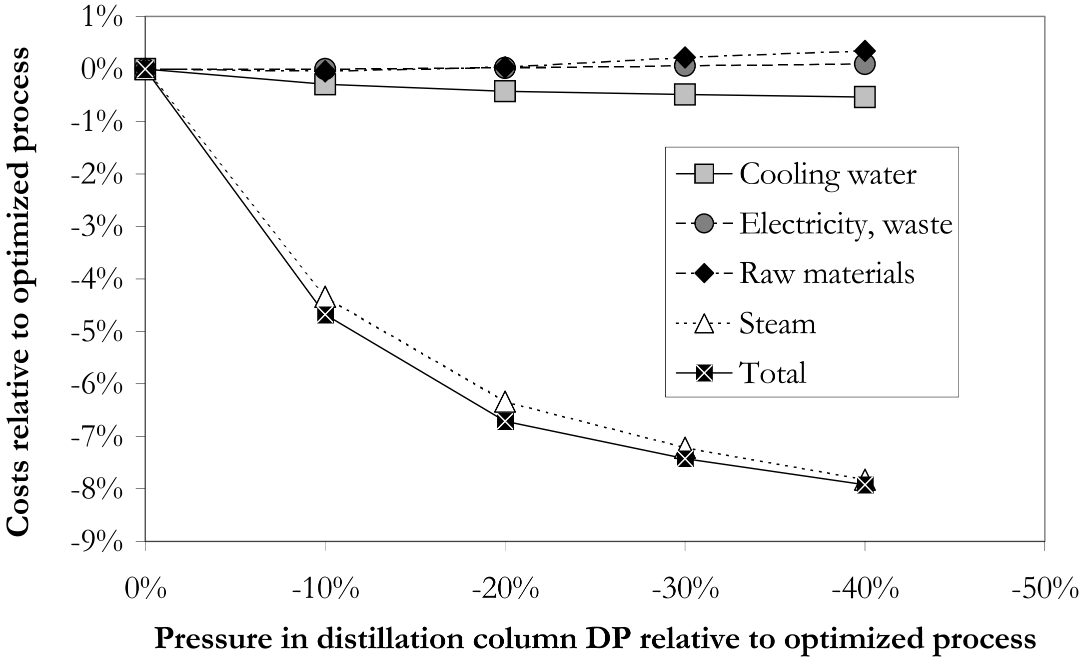


Figure 8-12: Variable process cost savings resulting from a pressure reduction in distillation column DP relative to the variable costs of the optimized process

reactant R1 (less than 1 wt%) of the final product stream. If the pressure in distillation column DP can be reduced to a pressure of approximately 1.2 bar, variable process cost savings in the order of 8% relative to the variable costs of the optimized process can be obtained.

If the pressure was further lowered the average temperature difference between the hot and the cold side in the column condenser would drop below 15°C. This indicates that either the required heat exchange surface would increase dramatically or that a colder cooling utility would be needed instead of the normal cooling water. Besides, if the pressure is lowered below 1.6 bar more extraction water will be needed and might lead to capacity limitations especially in extractor EX. Therefore, the cost optimum column pressure would have to be determined in a detailed profitability calculation.

8.3 Technical implementation of selected alternatives (Level 2)

8.3.1 Profitability calculation

In chemical engineering literature a large number of methods have been found on how to assess the profitability of investment projects related to chemical processes (Turton et al. (1998)**[63]**, Peters and Timmerhaus (1991)**[51]**). Since retrofit projects can bind considerable capital resources, it seems appropriate to take the time-value of money into account. Typical methods to assess the profitability of investment projects with respect to the time-value of future revenues and expenses (discounted profitability criteria) include:

- Net Present Value (*NPV*)
- Return on Investment (*ROI*)
- Internal Rate of Return (*IRR*)

Turton et al. (1998)**[63]** advocate the use of discounted profitability criteria for large retrofit projects as the accuracy to compare such types of projects with non-discounted profitability criteria can be insufficient[1]. In this thesis the *ROI* criteria is selected to assess the profitability of technical implementation scenarios for two structural retrofit alternatives. The *ROI* for a fixed time-period *TP* is defined as

$$ROI = \frac{\sum_{t=1}^{TP} C_t(1+r_t)^{-t}}{C_0} \cdot 100\% \qquad \text{(Eq. 8-1)}$$

The discount rate r_t in year t usually refers to the opportunity cost of capital and the economic risks involved in undertaking the project. The initial invest-

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[1] Non-discounted profitability criteria for investment projects include the Payback Period (*PBP*) and the Rate of Return on Investment (*ROROI*). For more information see Brealey and Myers (1996)**[6]** and Turton et al. (1998) **[63]**.

ment costs C_0 for the new equipment that is associated with the investigated retrofit project is estimated with up-to-date equipment prices and standard procedures such as Lang-Factors for the cost of installation (Lang (1947)[43] and (1948)[44]). The net cash-flow after taxes C_t in year *t* is calculated as follows:

$$C_t = (R_t - COM_t - dp_t)(1 - tr) + dp_t \qquad \text{(Eq. 8-2)}$$

In this equation, R_t represents the revenues in year *t* due to variable process cost savings and COM_t represents the cost of manufacturing in year *t* (e.g. new variable process costs associated with the new equipment) of the retrofit project. Further, dp_t symbolizes the yearly (linear) depreciation of the new equipment needed for the retrofit project while *tr* represents the income tax rate.

Three years is considered an acceptable time-period after which the *ROI*-value should have exceeded 100% (break even) in order to decide if the retrofit project is profitable enough or not. The same *ROI* criteria can also be used to compare alternative technical implementation scenarios with each other.

8.3.2 Pressure reduction in distillation column DI (FS8)

Variable process cost savings in the order of -12% relative to the optimized process are projected for a pressure reduction in distillation column DI to atmospheric pressure (see Figure 8-11). As described in Section 8.2.9 this pressure reduction almost exclusively reduces the steam and cooling water requirements of distillation column DI. Since the effects on the rest of the process are almost negligible the values of the optimization parameters in the optimized process of Section 7.5 are still considered optimal if the pressure is reduced in column DI. Therefore, these cost savings are viewed as the maximum attainable cost savings per year.

Although the pressure can be easily reduced in the distillation column, the lower pressure of its vapour distillate leads to a shorter residence-time in the following reactor RK2 which in turn leads to a lower conversion in that reactor. Thus, the pressure of the vapour distillate needs to be recompressed to 1.7 - 2.0 bar absolute pressure in order to maintain the desired conversion. The technical implementation scenario for this alternative is pictured in Figure 8-13 where compression plant C1 is used to recompress the vapor distillate of distillation column DI before it reaches mixer M2.

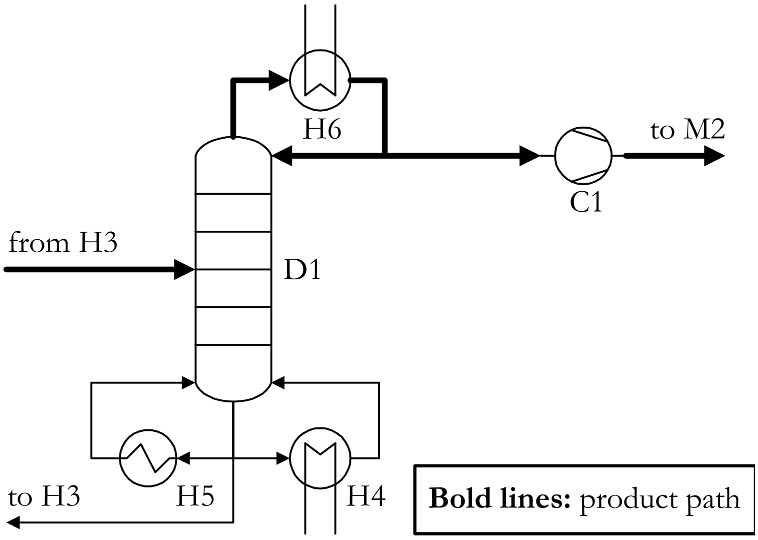

Figure 8-13: Technical implementation scenario for alternative FS8 (flowsheet refers to the master flowsheet of the Fine Chemical process in Figure 3-5 – see text for explanations)

The placement of the compression plant makes a building extension necessary. The compression plant could be installed in the building extension first and only connected to distillation column DI during the yearly routine plant shutdown (for maintenance reasons), which ensures that no production losses would occur during the installation. The 3-year *ROI* is calculated with *(Eq. 8-1)* and data from Table 8-2.

Table 8-2: Economic data for the profitability calculation on a technical implementation scenario for alternative FS8

Data	Value for Scenario[a]
Compression plant costs (120% design capacity)[b]	100 kUS$
Lang Factor for delivery and installation of equipment[c]	5
Costs for building extension (compression plant)	40 kUS$
Initial investment C_0 (Compression plant costs*Lang Factor + building)	540 kUS$
Yearly constant variable process cost savings (-12% – see text) R_t	516 kUS$
Yearly electricity costs for compressor COM_t	30 kUS$
Depreciation time for equipment (linear depreciation)	15 years
Depreciation time for building extension	40 years
Income tax-rate tr	0.25
Yearly net cash flow after taxes C_t (see *(Eq. 8-2)*)	366 kUS$
Discount rate (constant) r_t	0.15
3-year *ROI*	**155%**

a. Costs and cost savings are scaled by a confidential factor.

b. Investment costs estimated on the basis of a vendor's offer.

c. Average factor determined on past experience in the plant site.

The 3-year *ROI* for this scenario yields a value of 155%, which makes this retrofit project profitable according to the proposed decision criterion in the previous section.

8.3.3 Purge in distillation column DP (FS6)

Contrary to alternative FS8 in the previous section, a purge-stream from distillation column DP affects all unit-operations of the process. Therefore, depending on the side-draw flow-rate taken from distillation column DP, the structural simulation model needs to be re-optimized accordingly. Based on the results from the evaluation of alternative FS6 in Section 8.2.6 a purge scenario of 40 kg/h is optimized in the same manner as described in Section 7.5. Some optimization parameters in the optimized purge scenario exhibit slightly different values as compared to the optimized process (see Table 8-3).

Although only 40 kg/h are purged from distillation column DP the optimal reactant R1/R2 feed mass-ratio to reactor RK1 decreases considerably by 9.4% while the other changes are rather insignificant from an economic per-

Table 8-3: Differing values of optimization parameters between the optimized process and the optimized purge scenario

Optimization parameters (see Table 6-8 and Table 7-2)		Optimized purge scenario[a]
FP2 –	Reactant R1/R2 feed mass-ratio to reactor RK1	-9.4%
FP3 –	Reactant R2 recovery in the overheads of distillation column DI	+1.7%
FP6 –	Purities of reactants R1 and R2 in the overheads of distillation column DP	+2.9% R1, +2.1% R2
FP10 –	Water content in the overheads of distillation column DH	-12%

a. Values are given relative to the values of the optimized process.

spective. The variable process cost savings for the optimized purge scenario are calculated to be in the order of 1.7% as compared to the optimized process. Due to its composition the purge-stream has to be incinerated. Two possible scenarios are therefore investigated. In Scenario 1, it is assumed that the purge-stream is incinerated in an external incineration facility at no charge, yet without the possibility to obtain fuel credit. In Scenario 2, it is assumed that the purge-stream is incinerated in the incineration facility and that 85% of the fuel credit can be obtained. The fuel-credit is calculated with the average heat of combustion (1260 kJ/mol) of the purge-stream (66% of the usuable combustion heat generates mid pressure steam and 34% of the usuable combustion heat in the combustion gases replaces electrical power to heat reactor RK2) and yields additional 0.9% variable process cost savings. The technical implementation for both scenarios is shown in Figure 8-14.

Only minor additions have to made to the process plant. In the vicinity of stage 37 a pipe has to be welded to distillation column DP and the purge-stream buffered in a tank (T1). The necessary initial investment C_0 for the piping, the tank, the instrumentation and control devices, and the installation costs is roughly estimated at 100 kUS\$[1]. The 3-year *ROI*s are calculated for both scenarios with *(Eq. 8-1)* and data from Table 8-4.

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[1] This value is scaled by a confidential factor.

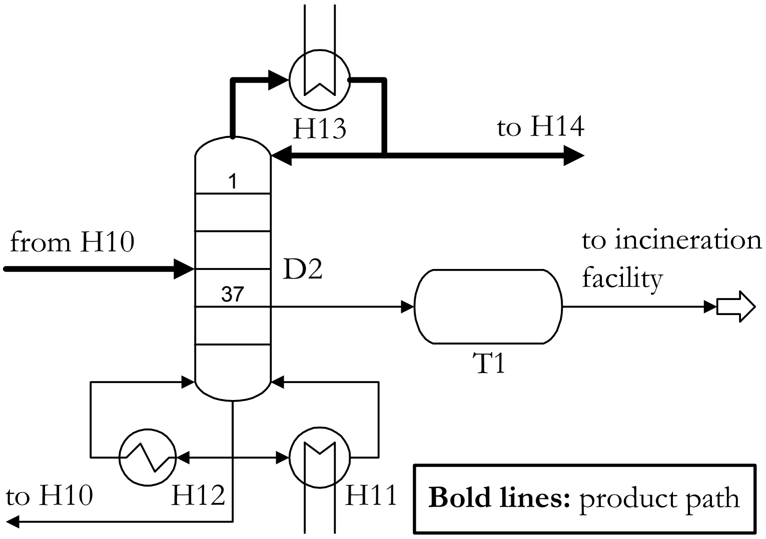

Figure 8-14: Technical implementation of both scenarios for alternative FS6 (flowsheet refers to the master flowsheet of the Fine Chemical process in Figure 3-5 – see text for explanations)

The scenarios exhibit profitable 3-year *ROI*s of 268% for Scenario 1 and 398% for Scenario 2. Even if costs were to arise from the incineration in an external facility the project would probably still be profitable.

Table 8-4: Economic data for the profitability calculation on two technical implementation scenarios for alternative FS6

Economic parameter	**Value for Scenario 1**[a]	**Value for Scenario 2**[b]
Estimated initial investment C_0	100 kUS$	100 kUS$
Yearly variable process cost savings R_t	154 kUS$	230 kUS$
Depreciation time for equipment (linear depreciation)	15 years	15 years
Income tax-rate *tr*	0.25	0.25
Yearly net cash flow after taxes C_t (see *(Eq. 8-2)*)	117 kUS$	174 kUS$
Discount rate (constant) r_t	0.15	0.15
3-year *ROI*	**268%**	**398%**

a. No benefits or costs arise from the incineration of the purge-stream. The costs and cost savings are scaled by a confidential factor.

b. Fuel credit is given for the incineration of the purge-stream (see text for explanations). The costs and cost savings are scaled by a confidential factor.

8.4 Discussion and conclusions

8.4.1 Discussion of the evaluation procedure

In the first level of the evaluation approach the attainable variable process cost savings that can be expected from the generated structural retrofit alternatives in Chapter 6 are calculated. Structural simulation models based on the optimization model previously described in Section 7.5 are used. Since at this stage the detailed technical implementation scenario(s) has (have) not yet been formulated the variable costs of the modified process cannot be minimized. This step in the evaluation procedure is only introduced so that the most cost reducing alternatives can be selected before the time-consuming process of generating technical implementation scenarios in the second level is undertaken. More specifically, it is believed that the alternatives with the highest attainable variable process cost savings without prior evaluation of the costs for the technical implementation scenarios (additional variable costs + investment costs) stand higher chances of being profitable. If the attainable cost savings of a given alternative are rather low and high investment costs can be anticipated in a technical implementation scenario, the alternative will most probably not be profitable. Of course alternatives with low cost savings and low investment costs can still be profitable, but will not generate large benefits in the long run.

8.4.2 Discussion of the results and conclusions

Although alternatives FS3, FS5, and FS7b are not evaluated up to the maximum possible variable cost savings (Sections 8.2.3, 8.2.5, and 8.2.8) the evaluation of the generated structural retrofit alternatives for the Fine Chemical process leads to the following conclusions:

[1] The results show that the maximum variable cost savings of alternatives FS2, FS3, FS4, FS6, and FS7a (0.7% to 1.6% relative to the variable costs of the optimized process) in the evaluation range are almost an order of magnitude lower than the cost savings of the remaining

alternatives FS1, FS5, FS7b, FS8, and FS9 (6% to 12% relative to the variable costs of the optimized process). Therefore, from an absolute point of view, the most interesting cost savings can be achieved with the latter alternatives. The profitability of a technical implementation scenario however depends on the required investment. Surprisingly, the pressure reductions in distillation columns DI and DP (alternatives FS8 and FS9) exhibit by far the highest cost savings. Even though alternative FS1 (increasing the conversion in reaktor RK1) seemed very promising judging by the total cost impact potential, the separation problem in distillation column DI (see Section 8.2.1) constrains the maximum variable cost savings considerably (only roughly 7% relative to the variable costs of the optimized process).

[2] It can be summarized from the results in this chapter that the low conversion in reactor RK1, the pressure above atmospheric level in distillation columns DI and DP, and the high accumulation of impurity-groups IG1 and IG2 in cycle path flows C1 and C2 are found to be the economically most eminent “problems” of the Fine Chemical process. In fact, the alternatives that aim at reducing the cycle path flow-rates of both impurity-groups exhibit a much higher economic performance than indicated by the total cost impact potentials. This is mainly due to the negative influence of the impurity-groups on the separation tasks in all three distillation columns DI, DP, and DH. Judging especially from the cost savings of alternatives FS7b the reduction of the flow-rates of impurity-group IG2 in the process has a slightly higher priority than of impurity-group IG1.

[3] Further, a qualitative discussion on the possible technical implementation scenarios for the generated structural retrofit alternatives also indicates that alternatives FS1, FS4, FS5, FS8, and FS9 require considerable investments into new equipment, while the remaining alternatives FS2, FS3, FS6, FS7a, and FS7b could be realized with rather low investment

efforts. However, alternatives FS3 and FS7b might cause important research costs for more selective catalysts in reactors RK1 and RK2.

Finally, technical implementation scenarios for two structural retrofit alternatives (FS6 and FS8) were investigated in a profitability analysis where a 3-year Return On Investment of at least 100% was used as profitability criterium. Two scenarios proposed for alternative FS6 (Section 8.3.3) result in 3-year *ROI*s of 268% and 398% and are therefore found to be particularly profitable. The single scenario proposed for alternative FS8 results in a 3-year *ROI* of 155% and can also be qualified as profitable.

9 SUMMARY, CONCLUSIONS, AND FUTURE RESEARCH

In this chapter a summary of the results of this thesis is given, conclusions are drawn, and future research is envisaged.

9.1 Summary of the key findings

9.1.1 Brief summary of the methodological work

This thesis proposes a new systematic screening method for the design of retrofit options that aim at improving the production cost-efficiency of a continuous process and supports decision making when selecting the most profitable options. The screening method follows an evolutionary approach and combines process insights, process-specific knowledge, and general engineering practice with mathematical analysis. It comprises three phases as described in Section 2.5:

[1] Analysis of the base case

[2] Generation of retrofit options

[3] Evaluation of the generated retrofit options

In the first phase, detailed mass and energy balances of a characteristic operational steady-state of the investigated process are established either by direct measurements in the existing plant or by process flowsheet simulation. The process is visualized using an appropriate graph representation and information from the mass and energy balances is attached to the vertices and edges of the resulting process graph accordingly. The process graph is then decomposed into open and cycle component path flows with their respective flowrates. At the end of the first phase, each component path flow is finally evaluated with an indicator framework that includes two indicators to measure economic performance (Material-value Added (*MVA*) and Energy & Waste Costs (*EWC*)) and two indicators to measure physico-chemical properties (Reaction Quality (*RQ*) and Accumulation Factor (*AF*)).

In the second phase, the most important component path flows from an economic perspective are systematically investigated using a list of generic retrofit actions that aim at an economic improvement of the process through retrofitting. The physico-chemical indicators are thereby used to pre-select appropriate generic retrofit actions from the complete list of actions. Applicable retrofit actions are selected for each component path flow. This procedure leads to the identification of important optimization parameters and the generation of structural retrofit alternatives – both referred to as retrofit options – to realize the desired retrofit actions. Lastly, the magnitude of the impact on the variable process costs is evaluated in a first approximation for each resulting retrofit options by calculating its total cost impact potential.

In the third and last phase, the identified optimization parameters are further studied by local sensitivity analysis in a process flowsheet simulator and the variable process costs minimized in a parameter optimization by manipulating the most cost sensitive optimization parameters. Undesirable process constraints encountered during local sensitivity analysis and the results of the parameter optimization are then used to generate additional structural retrofit alternatives. Further on, attainable cost savings are calculated by sensitivity analysis for all structural retrofit alternatives with regard to the previously optimized process as a benchmark. Finally, the alternatives that incur the highest cost savings are selected, detailed technical implementation scenarios are formulated on the basis of general engineering knowledge and experience, the parameters of the modified process are optimized with respect to variable process costs, and the profitability of each scenario is calculated. Based on these results the decision-maker can select the most profitable options.

9.1.2 Results of the HDA case study

The application of the screening method to the HDA case study yielded several retrofit options – six optimization parameters were identified to have an important impact on the economic performance of the process and four structural retrofit alternatives were formulated for the HDA process plant.

The same optimization parameters as cited in previous work by Fisher et al. (1987)[18] were identified. Fisher and co-workers also performed a sensitivity analysis on these parameters with regard to the total variable costs of the process. They found that especially the conversion in reactor RK and the purge flow-rate in vertex PU (see process graph in Figure 3-4) were an order of magnitude more cost sensitive than the other parameters. These findings could be confirmed in this thesis as the total cost impact potentials of these two optimization parameter were also found to be by far the most important ones of the six optimization parameters.

Among the structural retrofit alternatives the hydrogen/methane separation alternative (alternative HS1 – Table 6-5) yielded by far the highest total cost impact potential and was also part of the final MINLP cost-optimized flowsheet structure described by Kocis and Grossmann (1989)[37]. Alternative HS2 – increasing the heat exchange area or introducing a better cooling utility in vertex FL (see Figure 3-4) – was equally proposed to be realized in a retrofit project by Fisher and his co-workers in the aforementioned work. Although the total cost impact potential of that alternative scored second priority in the screening results, it resulted in a more than an order of magnitude lower total cost impact potential as compared to the hydrogen/methane separation alternative. Two more structural retrofit alternatives (alternatives HS3 and HS4) were generated in the screening method but resulted in even lower total cost impact potentials and were not reported in any one of the above mentioned publications, either.

9.1.3 Results of the Fine Chemical case study

In the case of the Fine Chemical process eight important optimization parameters were identified and seven structural retrofit alternatives were generated. Moreover, two additional structural retrofit alternatives were formulated due to the findings in the sensitivity analysis and parameter optimization. For obvious reasons the results of the screening method could not be compared to results reported in the literature. Instead, for validation purposes, they were investigated with rigorous process flowsheet simulations and compared with the findings of the plant engineers.

At first, based on the calculated total cost impact potentials, the optimization parameters in alternatives FP1-FP8 (see Table 6-8) appeared to be the most economically relevant parameters in the investigated process. It became apparent from the results of the sensitivity analysis in a process flowsheet simulator that optimization parameters FP1, FP2, FP4, and FP7 (conversion in reactor RK1, ratio of reactants R1 to R2 in the feed of reactor RK1, pressure in distillation column DI, and pressure in distillation column DP – see Figure 3-6) are the most cost-relevant parameters in this case study. A parameter optimization was then carried out in a process flowsheet simulator by manipulating selected optimization parameters based on the sensitivity results and resulted in significant variable cost savings (relative to the base case costs).

The total cost impact potentials for the nine generated structural retrofit alternatives indicate that alternatives FS1, FS8, and FS9 (see Table 8-1) appear to be the most economically important alternatives. In fact, these alternatives were confirmed to be among the economically most important alternatives (Chapter 8). However, some structural retrofit alternatives (alternatives FS3, FS5, FS6, and FS7) exhibited higher maximum attainable cost savings (see Section 8.2) than expected from their total cost impact potentials (see Table 6-9). This resulted from a highly non-ideal separation behaviour of the impurity-groups (see Section 8.4.2). Independently from this study, options FS1-FS3 and FS7-FS9 were identified as important structural retrofit alternatives by the process engineers of the investigated process.

Finally, technical implementation scenarios were proposed for two structural retrofit alternatives (FS6 and FS8). The profitability was calculated on the basis of a Return On Investment (*ROI*). Technical implementation scenarios were generated for alternative FS6 and FS8 and were found to be profitable.

9.2 Chances and limitations of the screening method

In this section conclusions on the chances and limitations of the proposed screening method are given with regard to the results from the two case studies. In parallel, a strong emphasis is also given to general conclusions on the structure of the screening method.

9.2.1 Chances

The screening method is a typical example of a divide-and-conquer-type strategy. This kind of solution strategy (or algorithm) represents a basic element of algorithms successfully applied to the field of computer science. The general principle consists in sub-dividing a complex problem into a number of simpler sub-problems and usually requires abstraction, idealization, and negligence of relationships among the sub-problems. Although there is a fair chance that some aspects of the master problem are lost by this procedure, the reduced complexity in each sub-problem facilitates the search for good solutions to each sub-problem which can later be aggregated again in the context of the master problem. In the screening method developed in this thesis the sub-problems consist of component path flows that contain a specific part of the information of the master problem concerning the whole process flowsheet. An advantage of the component path flow perspective as compared to the usually adopted unit-operation perspective consists in the fact that the new perspective is *problem-source*-oriented and has a strong focus on the interaction between the unit-operations. As an open component path flow originates in a supply flow of the process (by external feed to the process or by generation in a reaction) it describes the flow of material induced by this event with regard to different performance measures such as economics. In contrast, cycle path flows provide insights on the trade-offs between savings in raw material costs and energy costs for recycling. This representation is therefore designed to tackle the problem roots in the investigated process as identified by appropriate performance measures. It is commonly acknowledged that remediations at the problem source are found to be among the best solution options as stated by Fonyo et al. (1994)[19] on pollution prevention. In the case of the HDA process it could be demonstrated that this strategy led to the same optimization parameters and structural retrofit alternatives that were reported by Fisher et al. (1987)[18] and Kocis and Grossmann (1989)[37].

One of the main benefits of the screening method consists in guiding the decision-maker in a systematic manner through the step of analyzing the process (**Steps 3** and **4**) and generating retrofit options (optimization parameters and structural retrofit alternatives – **Step 5** of the screening method as shown in Figure 2-3). The decision-maker is thus forced to evaluate in a systematic manner a broad range of possible generic retrofit actions – although the list of actions can be certainly extended – that could be applied to the most economically relevant component path flows. Many retrofit options can be almost obvious from a direct inspection of the master problem. However, the advantage of a systematic screening bears the chance to find either not straightforwardly obvious potentials or potentials that are not judged to be important enough. A good example for this kind of situation was found in the analysis of the Fine Chemical process. It was commonly believed that the issue of the low conversion in vertex RK1 (see Figure 3-6) entailed the highest potential to improve the cost-efficiency of the process. Yet, the retrofit options to decrease the pressure in distillation columns DI and DP (alternatives FS8 and FS9 – see Table 8-1) proved to deserve much more attention, as a result of the screening, than was initially paid to them, even though these options were in fact known long before. Moreover, knowledge gathered during plant operations can be introduced in different steps of the screening method. Process-specific knowledge can be introduced in the calculation of the total cost impact potential of a retrofit option in **Step 5**, knowledge on process constraints can be included into the sensitivity analysis in **Step 6**, and engineering experience can be used in **Step 7** in order to generate technical implementation scenarios that achieve the desired cost savings with the minimum necessary investment.

Evaluating the component path flows with an indicator framework holds a number of advantages. In case of improving the cost-efficiency of a process the problem size can be effectively reduced by focussing only on the economically most important path flows ("cherry-picking"). Besides, the introduction of other physico-chemical indicators (Reaction Quality (*RQ*) and Accumulation Factor (*AF*)) yields additional information from a non-economic perspective. This information can be used to assist the decision-maker in selecting appropriate generic retrofit actions for each component path flow and to gain further insights of the problem-sources. It is also postulated that physico-chemical insights can act as a filter to initially constrict the search space for sensible retrofit actions before economics are even used to further constrict the search space. At any rate, the order of succession of the two filters is not deemed to be important as both orders would lead to the same results. The modularity of the indicator framework also allows for later introduction of other indicators that measure other performances in the process (e.g. for other retrofit incentives). Furthermore, the economic assessment (Material-Value Added (*MVA*) and Energy & Waste Costs (*EWC*)) leaves room for allocation preferences. In the calculation of the *MVA*-indicator the cost allocation factors (*CA*) should only be viewed as a proposition, since cost allocation is a considerable issue in economics and therefore should be left open to the judgement of the decision-maker. Also the allocation of energy costs to a component path flow could be performed on a non-physical basis (e.g. energy costs for a given unit-operation are only allocated to the component path flows that make the unit-operation necessary in the first place).

Time is a crucial factor in engineering practice. A number of aspects can be listed in favour of the screening method with respect to time savings. It is beneficial that **Steps 1** to **5** of the screening method can be carried out in a relatively short time-frame once mass and energy balances are available. The decomposition and assessment procedure (**Steps 3** and **4**) is well enough elaborated so that automatic computation with a minimum of interaction on behalf of the user is even possible. A process flowsheet simulator could be used to provide the required mass and energy balances. Since process optimization by manipulation of process operating parameters or by structural modifications of the plant are solution strategies that often are complementary to each other the simultaneous application of both retrofitting strategies in

Step 5 represents an advantage. Further, it could be shown in the case of the HDA process by comparison with results from Fisher et al. (1987)[18] that the most important optimization parameters could be determined without conducting a sensitivity analysis on all possible process operating parameters. Of course, more case studies would be needed in order to prove that **Step 5** is a valid procedure to determine the most important optimization parameters for a given process. Yet, the results suggest that evaluation time in the sensitivity analysis (**Step 6**) can be saved by a good pre-selection of relevant optimization parameters. Finally, detailed and time-consuming rating calculations for equipment only have to be performed in the last step of the screening method when the solution space for structural retrofit alternatives has been reduced accordingly.

9.2.2 Limitations

As with any method the proposed screening method also shows a number of limitations. A minor disadvantage consists in the fact that the retrofit incentive has to be known in advance. Nevertheless, it is argued that the retrofit incentives are almost evident in response to changing external or internal conditions such as increasing market demand (capacity expansion is the logical consequence), increasing competition (profit margin decreases, which makes an improvement of cost-efficiency necessary), lowered emission limits on specific substances (minimization of the rate of emission necessary), and others.

A major drawback consists in the fact that the method does not include retrofit incentives other than improving the cost-efficiency so far and does not address the issue on how to deal with potentially conflicting incentives in case retrofitting multiple retrofit incentives are envisaged (e.g. improving cost-efficiency and improving the ecological impact of a process). The review on retrofitting (Section 2.1) yet clearly indicates the prime importance of retrofit design for capacity expansion. However, the method leaves open the possibility of defining new performance indicators for other retrofit incentives in the analysis phase.

The screening method is objective throughout the analysis phase (**Steps 1** to **4** – see Figure 2-3). Nonetheless, allocation rules for the path flow assessment procedure have to be decided upon and the generation phase for retrofit options in **Step 5** are highly subjective as it heavily relies on the judgement of the decision-maker. Therefore the retrofit options generated by the screening method are quite dependent on the decision-maker's understanding of the cause-effect relationships present in the investigated process.

Another inconvenience consists in the fact that targets for the attainable cost savings of a structural retrofit alternative cannot be safely established in the proposed screening method without the use of rigorous simulation. The total cost impact potential does indicate the order of magnitude of the cost savings. But the application of the screening method to the Fine Chemical process showed that the impact potentials for the structural retrofit alternatives were quite imprecise in predicting their attainable cost savings. The inherent problem lies in non-linearities of the process which make linear extrapolation unreliable in the calculation of the total cost impact potentials.

A further disadvantage consists in the fact that heat integration is not included in the generation phase of the screening method (Step 5). Heat integration is only considered after the application of the screening method and is hence treated as a kind of final stage technique.

Another drawback is the lack of a systematic procedure in the decision phase in **Step 7** on how to evaluate the use of different retrofitting strategies such as repiping, modification or replacement of existing equipment, and addition of new equipment. So far, this step is quite empirical and solely relies on the experience of the decision-maker.

In its present structure, discontinuous processes cannot be studied with the proposed screening method because the decomposition procedure requires a steady-state operation. More-over, discontinuous processes are generally subject to different cost structures as compared to continuous processes (e.g. costs for non-occupation time in a multi-purpose plant) which would thus require a modification of the economic indicators of the screening method.

Finally, the chemical reaction scheme is implicitly assumed to be unchangeable. On the one hand this simplifies the generation of retrofit options in the screening method. On the other hand this assumption considerablly constricts the search space for retrofit options.

9.3 Scope and applicability of the screening method

Some important elements of the introduced screening method follow a similar line of thoughts as exploited by well-established methods in industry such as Value Engineering (Brown (1992)[7]) and Hazard Analysis and Operability Studies (HAZOP – Lawley (1974)[45]). Value Engineering was originally developed by L. D. Miles in the late 40's at General Electrics as a method to reduce production costs. The principle consists in decomposing a given product into the basic functions it fulfils (e.g. functions targeted at product use, life expectancy, quality) and allocates production costs to each of these functions on the basis of subjective judgement. Upon these results decisions can be made whose functions might be superfluous and should be removed from the product in order to reduce its production costs. In principle, the concept of decomposing a process flowsheet into component path flows and evaluating each path flow individually in **Steps 3** and **4** of the screening method (see Figure 2-3) is similar to the concept of Value Engineering. The HAZOP-method was initially developed by ICI in the late 60's and intended for the systematic investigation of process safety of new and existing processes. The core principle of the HAZOP-method consists in studying possible deviations in process operating conditions with generic *guidewords* in order to identify their causes, consequences, and adequate process measures required to deal with them. In the screening method, the concept of generic retrofit actions shares similarities with the guideword-concept of the HAZOP-method.

Most methods applied in industrial practice are team-oriented so that specific knowledge and experience can be included during problem analysis, development of solutions and decision-making. As the generation of retrofit options (**Step 5**) is a crucial step in the screening method, the author proposes to generate retrofit options by team work and use well-known creativity techniques such as brainstorming, morphology, and others in conjunction with the described procedure in this step. Even though an application of the screening method does not guarantee to find better solutions than the ones that would be found by an experienced engineer on an ad hoc basis, its systematic nature increases the chances of finding the best possible alternatives. In the present form the screening method is only applicable to continuous processes dedicated to the production of single products and is therefore mostly interesting for the petrochemical and basic chemical (commodities) sectors of the chemical industry.

The screening method presented can be used along the whole process life-cycle as changes, e.g. on the market or in regulations, force chemical industry to redesign their plants numerous times in their life-times. It bears the potential to collect and integrate gathered process-specific knowledge during the process life-cycle and could be used as a communication tool for process engineers when dealing with a specific process. For instance, new available technologies on the market could be analyzed in perspective of already generated retrofit options in the past, or safety studies like HAZOP could be simplified with component path flow information and process insights from the method.

9.4 Future research

9.4.1 Extension of the screening method to retrofitting discontinuous processes

Discontinuous processes (batch and semi-batch) are typically operated in two different types of facilities. If large production capacities are needed but the discontinuous process cannot or has not been transformed into a continuous process, production is most often carried out in a plant uniquely designed for that specific product (mono plant). In case smaller production capacities are desired discontinuous processes are generally operated in production campaigns in a multi-purpose or a multi-product plant. The screening method principle and its structure could be certainly applied to the former type of discontinuous processes (mono plant) since the equipment is fixed and constantly used for the production of the same product.

However, retrofit design has a completely different meaning when discontinuous processes are operated in a multi-purpose-plant. As already explained, the production of different products in a multi-purpose plant is organized in campaigns. Before each campaign starts the production recipe has to be defined for the desired product. Since multi-purpose plants typically comprise a large number of equipment items (e.g. reaction vessels, storage tanks, filters, centrifuges, and dryers) a good arrangement of equipment items regarding space-time yield has to be found prior to each campaign. Typically, the arrangement is then improved from campaign to campaign in case the optimal arrangement was not readily found in the first run. In that sense, retrofit design of a *single* discontinuous process operated in a multi-purpose plant is reduced to only one strategy: repiping. This subject is also known as *batch scheduling* and extensively studied in literature. Sometimes old equipment of a multi-purpose plant is decommissioned or new equipment added, which represents two further retrofitting strategies according to the definition introduced by Grossmann et al. (1987)**[24]**. Yet, the difference as compared to retrofit design on continuous processes consists in the fact that these strategies are only considered if a sufficient number of discontinuous processes can be operated in a more profitable manner due to changes in equipment. Therefore, those additional strategies are only applicable to retrofitting of *multiple* discontinuous processes. In the light of these findings, the proposed screening method seems hardly suited for retrofit design on discontinuous processes operated in multi-purpose plants. Instead optimization approaches might be more suited.

9.4.2 Multiple retrofit incentives

The screening method presented so far only tackles the retrofit incentive of improving the production cost-efficiency of continuous processes. As described earlier in Section 1.2 a considerable number of other retrofit incentives exist, i.e. capacity expansion, improvement of environmental performance, improvement of process safety, and improvement of flexibility among others. The survey conducted by the Chemical Manufacturers Association (CMA)[10] (see Section 2.1) indicates that especially systematic retrofit design methods for capacity expansion are of major interest because of the considerable capital expenditures for that specific retrofit incentive. The modularity of the indicator framework of the screening method for the analysis of retrofit potentials could be extended to encompass other retrofit incentives. In the following, general leads on how to deal with other retrofit incentives in the context of the screening methods are given:

- **Capacity expansion:** The objective in retrofit design for capacity expansion consists in maximizing the throughput of product while minimizing the capital investments required. In the analysis phase of the screening method (**Steps 1** to **4** – see Figure 2-3) an adequate performance measure should be able to indicate the maximum flow-rate increase of each component path flow until the capacity limit of any of the unit-operation(s) along the path flow is reached. Such an indicator has two advantages, i.e. it could highlight the bottlenecks of the process and it could indicate how to modify single component path flows other than simply increasing the overall feed of raw materials to the process. This indicator would require the knowledge of the maximum capacity of each equipment which could be provided by calculation, plant experiments, or operational experience. The same indicator could also be used to deal with another retrofit incentive, i.e. the improvement of operational flexibility.
- **Improvement of environmental performance:** Eco balances have emerged as a tool to assess the environmental impact with respect to process inputs but are dependent on good environmental inventory data for each component (inventory of primary resources needed to produce a component). The objective in retrofit design for environmental performance should be to minimize the overall ecological impact of the process. An indicator could be framed for the analysis phase of the screening method in order to calculate the eco balance of each component path flow. Conclusions could then be drawn from that information on how to

modify the process in order to minimize the overall economic impact of the process.

- **Improvement of health and safety in production:** Koller et al. (2000)[38] previously introduced an indicator framework to assess processes with respect to environmental, health, and safety criteria (EHS). A part of the indicator framework of this method could be used to evaluate and improve health and safety issues on the basis of component path flows in the analysis phase of the screening method.

9.4.3 Generation and rough evaluation of structural retrofit alternatives

In **Step 5** of the screening method (see Figure 2-3) the decision-maker generates structural retrofit alternatives based on generic retrofit actions, process-specific knowledge, and general engineering knowledge. This section highlights a number of leads on improving the generation and rough evaluation of structural retrofit alternatives:

- **Generic retrofit actions:** In principle, the proposed generic retrofit actions represent heuristic rules specifically targeted at the retrofit design of processes. An extensive number of heuristic rules in the context of grassroot design of processes have been reported in literature after they were initially introduced by Douglas (1985)[12]. A systematic study of the existing heuristic rules could reveal further generic retrofit actions that could be used in the retrofit design context.
- **Pre-selection of structural retrofit alternatives:** Grassroot design of separation systems by inspection of physico-chemical properties (also known as *thermodynamic insights*) was introduced by Barnicki and Fair (1990)[1], Barnicki and Fair (1992)[3], and Jaksland et al. (1995)[34] in order to find the optimal design of a separation system for a given separation task. During application of the screening method, proposed in this thesis, generic retrofit actions can sometimes indicate the utility of introducing alternative separation techniques (if they are more cost-effective (Kürüm et al. (1998)[42])). The principle of separation design based on

thermodynamic insights could be included in the method in order to find feasible alternative separation techniques.

- **Rough evaluation of structural retrofit alternatives:** As concluded in the previous chapter the total cost impact potential of a structural retrofit alternative can only be viewed as an order-of-magnitude estimation of the attainable cost savings. Hence, it would be desirable to refine this indicator so that maximum cost savings targets can be calculated. Such an indicator could then be used effectively to reduce the number of structural retrofit alternatives to be studied in the detailed evaluation procedure described in **Step 7** of the screening method.

9.4.4 Generation and detailed evaluation of technical implementation scenarios

One of the limitations of the presented screening method that were mentioned in the previous chapter consists in the lack of a systematic procedure to generate technical implementation scenarios for the structural retrofit alternatives in **Step 7**. A systematic procedure that addresses the four types of retrofitting strategies according to Grossmann et al. (1987)**[24]** – repiping, modification of existing equipment, replacement of existing equipment, and addition of new equipment – could effectively assist the decision-maker in this task. However, since retrofit design is also very plant-specific it is believed that such a procedure needs to be highly interactive and cannot be fully automated. Besides, the question should be raised, if such a task needs to be completely automated anyhow. In fact, the decision-maker always needs a certain degree of freedom in order to face decisions in the specific problem context.

After technical implementation scenarios have been formulated for the selected structural retrofit alternatives in **Step 7** of the screening method, the required investment costs have to be estimated by the decision-maker for each scenario. In grassroot design a number of estimation procedures with varying degrees of accuracy can be found in literature, of which a good overview is given by Peters and Timmerhaus (1991)**[51]**. Yet, the estimation of investment costs for technical implementation scenarios is much more complex and has to be carried out by an experienced process engineer for each project in a time-consuming procedure. Hence, there is a need for a systematic procedure that simplifies at least the calculation of preliminary investment estimates so that the generated scenarios can be quickly assessed on their profitability.

NOTATION

LATIN SYMBOLS

A	Energy allocation factor, [-]
AF	Accumulation factor indicator, [-]
$\bar{B}$	Edge-vertex incidence matrix of the sub-graph, [edges*vertices]
C	Yearly net cash flow after taxes, [kUS$]
C_0	Initial investment for a retrofit project at time 0, [kUS$/a]
CA	Cost allocation factor, [-]
COM	Yearly cost of manufacturing, [kUS$]
$\bar{D}$	Cycle-edge incidence matrix, [cycles*edges]
$\vec{d}$	Total demand flow-rate vector of all vertices of the sub-graph, [kg/h]
d	Single vertex demand flow-rate, [kg/h]
dp	Yearly depreciation of the new equipment for a retrofit project, [kUS$]
E	Effect of a component path flow on a reaction *rk*, [-]
EC	Energy cost indicator, [kUS$/a]
EWC	Energy and waste cost indicator, [kUS$/a]
F	Sum of all input mass flow-rates to a vertex, [kg/h]
$\vec{f}$	Edge flow-rate vector of the complete process graph, [kg/h]
f	Edge flow-rate, [kg/h]
M	Molecular weight, [kg/kmol]
MVA	Material value-added indicator, [kUS$/a]
m	Component path flow-rate, [kg/h]
n	Molar flow-rate, [kmol/h]
p	Pressure, [MPa]
PE	Price of a utility, [US$/GJ]
PP	Specific value of a path flow, [US$/kg]
PR	Price of a raw material, [US$/kg]
Q	Energy duty of a sub-operation, [kW]

R	Yearly revenues (variable cost savings) from a structural retrofit alternatives, [kUS$]
ROI	Return on Investment, [%]
RQ	Reaction quality indicator, [-]
r	Discount rate, [-]
S	Selectivity (ratio of molar flow-rate of desired product to molar flow-rate of undesired product leaving the investigated reactor), [-]
$\vec{s}$	Total supply flow-rate vector of all vertices of the sub-graph, [kg/h]
s	Single vertex supply flow-rate, [kg/h]
T	Temperature, [°C]
tr	Tax rate, [-]
TVA	Total value-added indicator, [kUS$/a]
V	Volumetric flow-rate, $[\mathrm{m}^3/\mathrm{h}]$
WAC	Waste cost allocation factor by concentration, $[(\mathrm{US\$m}^3)/\mathrm{kg}]$
WAM	Waste cost allocation factor by mass, [US$/kg]
WAV	Waste cost allocation factor by volume, $[\mathrm{US\$/m}^3]$
WC	Waste treatment cost indicator, [kUS$/a]
w	Flow distribution factor, [-]
$\vec{x}$	Vector of maximum component cycle flow-rates, [kg/h]
X	Reaction conversion, [-]
y	Component edge flow-rate fraction, [-]

GREEK SYMBOLS

ν	Stoichiometric coefficient, [-]
ξ	Extent of a reaction, [kmol/h]
ρ	Density, $[\mathrm{kg/m}^3]$

SUBSCRIPTS

a	Index of edges positively incident with a vertex, $\{1, ..., M\}$
b	Index of edges negatively incident with a vertex, $\{1, ..., N\}$
fp	Index of desired products of the process, $\{1, ..., FP\}$
i	Index of vertices, $\{1, ..., I\}$
ip	Index of feed flows (non-edge flows) to a vertex, $\{1, ..., IP\}$
ir	Index of supply flows due to a reaction in a vertex, $\{1, ..., IR\}$
j	Index of edges in the complete process graph, $\{1, ..., J\}$
k	Index of cycle and open path flows of a component, $\{1, ..., K\}$
o	Index of open path flows of a component, $\{1, ..., O\}$
op	Index of output flows (non-edge flows) from a vertex, $\{1, ..., OP\}$
or	Index of demand flows due to a reaction in a vertex, $\{1, ..., OR\}$
out	Output edge flow where component path flow k stops
pd	Index of products generated in a gross reaction equation, $\{1, ..., PD\}$
r	Index of reactive unit-operations of a component path flow, $\{1, ..., R\}$
rk	Index of reactions in reactive unit-operation r affected by component path flow k, $\{1, ..., RK\}$
m	Arithmetic mean value (input and output value of a sub-operation)
u	Index of sub-operations along a component path flow, $\{1, ..., U\}$
uk	Index of component path flows involved in a sub-operation, $\{1, ..., UK\}$
t	Index of years for the ROI calculation, $\{1, ..., TP\}$
z	Index of cycle path flows, $\{1, ..., Z\}$

SUPERSCRIPTS

c	Component index
rm	Index of raw materials involved in a gross reaction scheme to generate component c, $\{1, ..., RM\}$

MATHEMATICAL OPERATORS

diag	Diagonalisation of a vector

SETS

CP	Set of vertices forming a cycle path
PG	Set of all vertices of the complete process graph
SC	Set of components flowing in the sub-graph
SG	Set of all sub-graph vertices

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APPENDIX

A.1 Important design data: HDA case study

The most important operating parameters used in the simulation of the selected HDA process alternative and prices for raw materials, utilities, waste disposal, and products are displayed in Table A-1.

Table A-1: Important data for the HDA case study

Feedstock/product	**Comment**	**Price [US$/kg]**
Hydrogen feed	95 vol% H_2, 5 vol% CH_4, 38 bar	2.0
Toluene feed	100% toluene, 1 atm	0.30
Benzene product	99.97 mol% benzene	0.44
Utilities	**Comment**	**Price**
Natural gas	-	0.025 US$/kWh
Electricity	-	0.047 US$/kWh
Cooling water	-	0.1 US$/$m^3$
Steam	Produced by process waste incineration – fuel credit (70% of heat of combustion assumed)	12 US$/t
Most important operating parameters[a]		
Plant design capacity		100000 t/a
Reactor (RK)	Temperatures	621°C/670°C (inlet/outlet)
	Average pressure	36 bar
	Hydrogen/toluene molar ratio	5.5
Fired heater (FH)	Heat duty	8.7 MW
Quench & flash drum (H3 & FL)	Cooling duty	6.0 MW
Flash drum (FL)	Flash temperature	38°C
	Flash pressure	33 bar
Purge stream (PU)	Hydrogen molar fraction	0.46
Stabilizing column (D1)	Reflux ratio/pressure	1.0/10 bar
	Number of stages	25
Benzene column (D2)	Reflux ratio/pressure	1.3/1 atm
	Number of stages	55
Toluene column (D3)	Reflux ratio/pressure	1.0/1 atm
	Number of stages	20

a. The operating parameters refer to the HDA process flowsheet in Figure 3-3.

A.2 Data for energy cost allocation: HDA case study

In this section, the data required for the calculation of the *EWC*-indicator is presented in Table A-2.

Table A-2: Data for energy cost allocation in the HDA case study

Equipment[a]	**Sub-operation** u	**Net energy duty** Q_u **[kW]**	**Utility type**	**Mean temp.** T_m **[°C]**	**Mean pressure** p_m **[bar]**	**Allocation factor**[b] A_u
Pumps & Compressor						
P1	Compressing	37	Electricity	28	20	Density (l)
P2 (negligible)	-	-	-	-	-	-
P3	Compressing	19	Electricity	113	20	Density (l)
C	Compressing	356	Electricity	48	35	Density (g)
Heaters & Coolers						
H10	Heating	8680	Natural gas	522	38	Heat capacity (g)
H3	Cooling	561	Cooling water	163	34	Heat capacity (g)
FL[c]	Condensing	2010	Cooling water	96	33	Heat of vaporization
	Cooling	3480	Cooling water	96	33	Heat capacity (g)
Condensers						
H5	Condensing	137	Cooling water	37	10	Heat of vaporization
H7	Condensing	3030	Cooling water	98	1.01	Heat of vaporization
H9	Condensing	1060	Cooling water	110	1.01	Heat of vaporization

a. The equipment acronyms refer to the nomenclature used in Figure 3-3.

b. The acronyms in brackets refer to gas phase (g) and liquid phase (g).

c. Two sub-operations occur in flash-unit FL: Condensing and cooling.

A.3 Mass balance data: HDA case study

In this section, detailed mass balances of the HDA process are presented in Table A-3.

Table A-3: Mass balances of the HDA process (acronyms refer to the process flowsheet in Figure 3-3)

To:	C	M1	P1	FL	H10	H2	H3	RK	D3	D1	PU	H2	-	H1	D2	-	-	P3	M1	-	M1	M1
From:	PU	-	-	H3	H2	M1	H2	H10	D2	FL	FL	H1	PU	RK	D1	D1	D3	D3	P1	D2	P3	C
Mass flow [kg/h]																						
Benzene	742	0	0	13497	868	868	13497	868	126	12631	866	13497	124	13497	12622	9	0	126	0	12496	126	742
Toluene	93	0	15386	5122	20488	20488	5122	20488	5009	5014	108	5122	16	5122	5014	0	0	5009	15386	4	5009	93
Hydrogen	1816	638	0	2122	2453	2453	2122	2453	0	3	2120	2122	304	2122	0	3	0	0	0	0	0	1816
Diphenyl	0	0	0	487	94	94	487	94	487	487	0	487	0	487	487	0	393	94	0	0	94	0
Methane	16795	267	0	19738	17062	17062	19738	17062	0	131	19606	19738	2811	19738	0	131	0	0	0	0	0	16795
Mass fraction [-]																						
Benzene	0.04	0.00	0.00	0.33	0.02	0.02	0.33	0.02	0.02	0.69	0.04	0.33	0.04	0.33	0.70	0.07	0.00	0.02	0.00	1.00	0.02	0.04
Toluene	0.00	0.00	1.00	0.13	0.50	0.50	0.13	0.50	0.89	0.27	0.00	0.13	0.00	0.13	0.28	0.00	0.00	0.96	1.00	0.00	0.96	0.00
Hydrogen	0.09	0.70	0.00	0.05	0.06	0.06	0.05	0.06	0.00	0.00	0.09	0.05	0.09	0.05	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.09
Diphenyl	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.09	0.03	0.00	0.01	0.00	0.01	0.03	0.00	1.00	0.02	0.00	0.00	0.02	0.00
Methane	0.86	0.30	0.00	0.48	0.42	0.42	0.48	0.42	0.00	0.01	0.86	0.48	0.86	0.48	0.00	0.92	0.00	0.00	0.00	0.00	0.00	0.86
Total flow [kmol/h]	1958	333	167	2515	2515	2515	2515	2515	59	229	2286	2515	328	2515	219	10	3	57	167	160	57	1958
Total flow [kg/h]	19445	905	15386	40966	40966	40966	40966	40966	5622	18266	22700	40966	3255	40966	18122	143	393	5229	15386	12500	5229	19445
Total flow [m3/h]	1579	225	18	2672	3801	1652	2695	5022	7	22	1805	5071	264	5721	29	25	1	7	18	16	7	1407
Temperature [°C]	38	38	25	155	422	55	171	621	131	38	38	563	38	670	221	37	255	110	30	98	116	57
Pressure [bar]	32.1	38.3	1.0	33.4	38.3	38.3	34.5	37.2	1.0	32.8	32.8	34.5	32.1	34.5	10.0	10.0	1.0	1.0	38.3	1.0	38.3	38.3

A.4 Measured and simulated mass balances: Fine Chemical case study

In this section the simulated component mass balances are compared with the measured component mass balances from the existing production plant and shown in Table A-4. It should be noted that the measured component mass balances are not consistent probably due to a number of reasons such as fluctuations of operating conditions in the plant, errors in measurements of mass flow-rates, and measurement errors on component concentrations in samples among others.

With two exceptions the deviations of the simulated mass flows do not exceed ±30% from the measured mass flows. Especially coupled product CP and impurity-groups IG1 and IG2 exhibit the highest deviations. In the case of CP, calculations on the reaction extent with respect to the other components involved in the main reaction *(REq. 3-3)* of reactor RK1 indicates that the CP concentrations were rather inaccurate. In the case of IG1 and IG2, the measured flows are highly inconsistent (mass conservation). For simulation purposes these inconsistencies were eliminated by means of least-squares minimization.

Table A-4: Comparison of measured and simulated mass flows: Fine Chemical case study

		Components[a]						
Edge flow[b]	**Simulated mass flows[c] and deviations from measured mass-flows**	**R1**	**R2**	**I**	**P**	**CP**	**IG1**	**IG2**
$f_{MI1,RK1}$	Simulated mass-flow [kg/h]	887	2447	42	11	6	103	53
	Deviations [%]	-3.1	+3.9	+30.7	-0.2	-26.8	+10.9	-1.9
$f_{RK1,DI}$	Simulated mass-flow [kg/h]	488	2008	764	0	128	103	59
	Deviations [%]	-1.3	+5.0	-5.1	-	+29.8	+6.1	-5.1
$f_{DI,DH}$	Simulated mass-flow [kg/h]	0	780	0.2	0	128	3	31
	Deviations [%]	-	+5.4	-100	-	+30.4	-92.9	-13.9
$f_{DI,MI2}$	Simulated mass-flow [kg/h]	488	1229	722	0	0	100	28
	Deviations [%]	-1.6	+4.9	+0.9	-	-	+6.5	-4.1
$f_{MI2,RK2}$	Simulated mass-flow [kg/h]	525	1239	1520	0	0	108	32
	Deviations [%]	+0.5	+5.1	+0.1	-	-	+7.2	-2.3
$f_{RK2,DP}$	Simulated mass-flow [kg/h]	546	1683	42	1001	0	111	23

Table A-4: Comparison of measured and simulated mass flows: Fine Chemical case study

		Components[a]						
Edge flow[b]	**Simulated mass flows[c] and deviations from measured mass-flows**	**R1**	**R2**	**I**	**P**	**CP**	**IG1**	**IG2**
	Deviations [%]	+1.8	+6.7	+1.6	+0.4	-	+20.4	-9.2
$f_{DP,MI1}$	Simulated mass-flow [kg/h]	535	1574	42	10	0	100	23
	Deviations [%]	+5.7	+4.7	+5.2	+3.3	-	+27.4	-1.1
$f_{DP,EX}$	Simulated mass-flow [kg/h]	11	109	0	991	0	12	0
	Deviations [%]	+6.3	+15.0	-	-0.4	-	-2.1	-

a. Mass flows of by-product B could not be measured in the existing plant due to its high volatility (difficult sampling technique).

b. Refers to the Fine Chemical process graph in Figure 3-6.

c. Values of the simulated mass-flows are scaled by a confidential factor.

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