Chemical Engineering and Processing 109 (2016) 39–50

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Design and intensification of industrial DADPM process

Anne M. Benneker[a,1], Louis G.J. van der Ham[a], Bart de Waele[b], Arend Jan Zeeuw[b], Henk van den Berg[a,*]

[a] Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Drienerlolaan 5, 7522 NB, Enschede, The Netherlands[2]
[b] Huntsman Holland B.V., Merseyweg 10, Botlek, 3197 KG, Rotterdam, The Netherlands

ARTICLE INFO

Article history:
Received 4 May 2016
Received in revised form 15 July 2016
Accepted 20 August 2016
Available online 21 August 2016

Keywords:
Computer aided process intensification
Industrial application

ABSTRACT

Process intensification is an essential method for the improvement of energy and material efficiency, waste reduction and simplification of industrial processes. In this research a Process Intensification methodology developed by Lutze, Gani and Woodley at the Computer Aided Process Engineering Center (CAPEC) at DTU in Denmark is used for the intensification of the 4,4′-methylenedianiline (DADPM) process at Huntsman B.V. in the Netherlands. The goal of this research was the extension of the DTU methodology for applicability on running, industrial processes and improvement of the Huntsman process, focus is on reduction of operation costs. We have shown in the DADPM case that an analysis of the performance per section or unit operation and the mutual interactions provide essential additional information that is not being detected by the DTU method. We demonstrated how good engineering practice and heuristics can also reduce the number of process options that have to be modelled in detail. Selection of the optimal process is done based on a quantitative analysis of several intensified process options which all obey all required constraints. Equipment models were built in Excel and integrated in an Aspen Plus process flowsheet containing 27 different process options. A sensitivity analysis is done using Aspen, yielding the optimized and intensified process for DADPM production. Energy costs for the DADPM process are reduced by 24% using a combination of both heuristic and methodology-based intensification. We conclude that the method developed by Lutze et al. is a valuable tool for PI and process analysis and synthesis. The extension developed using heuristics, provides additional insight, traces the process weak points, facilitates implementation of new technology and reduces calculations.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Process intensification is a method and principle that can be used for improving chemical processes, yielding a process with increased material, energy and waste efficiency [1–3]. The principle of process intensification is first mentioned in the 1970's [4,5], but gained more interest in the late 1990's as the need for sustainable and safe process developments increased. The definition of process intensification (PI) has changed over the years and is still subject of discussions in literature [1–3,6–8]. PI can be viewed as a tool as well as a more general principle for improvement of both existing and new chemical processes. As raw materials and energy become scarcer it is important to find more efficient ways to produce desired products in the chemical industry and process intensification could be of use in reducing waste material and energy streams. Many different approaches of process intensification can be pursued. Reduction in equipment size is one well known way of process intensification, in which the field of microfluidics will become increasingly important [9]. Different emerging types of equipment are used for reduction of equipment size, e.g. Higee distillation and microwave reactors [1,4,10]. PI can also be achieved by integration of process tasks and equipment and process heat integration. Due to the various goals that can be achieved by several methods of intensification it is difficult to define process intensification by one single sentence. Several different authors propose different definitions, mostly overlapping and almost in accordance but slightly altered from the definitions proposed before [1–8]. Almost all definitions indicate a

---

Abbreviations: DTU, Danish Technical University; FRI, Feed, Reactor and Isomerization; NFS, Neutralization and First Separation; DADPM, 4,4′-Methylenedianiline; PI, Process Intensification; NPO, Number of Process Options; PS, Process Steps; NIU, Number of Identified Units.

[*] Corresponding author.
E-mail address: h.vandenberg@utwente.nl (H. van den Berg).

[1] Current address: Soft Matter, Fluidics and Interfaces Group, Faculty of Science and Technology, University of Twente, Enschede, The Netherlands. http://www.utwente.nl/tnw/sfi/.

[2] http://www.utwente.nl/tnw/spt/.

http://dx.doi.org/10.1016/j.cep.2016.08.009
0255-2701/© 2016 Elsevier B.V. All rights reserved.

substantial improvement on the process, some focus on the costs and some focus on sustainability. Differences in view on PI reflect the variety of its applications in industry. Some think of PI as replacement of unit-equipment by improved PI equipment while others would like to apply PI to a complete process to achieve an optimization in the entire process instead of the unit operations. A more detailed discussion on the definition can be found in the first chapter of the thesis of Lutze [5].

Several groups perform research in different areas of process intensification. The aim of Andrzej Stankiewicz at TU Delft is to develop new concepts of "perfect" chemical reactors and separation systems. His team develops new methods and related equipment to influence and control molecular interactions (orientation, forces and energies) in systems, in which such interaction play crucial role, including reactions, distillation and crystallization. For this program microwave technologies are used [11]. The team in Leuven led by Ton van Gerven does PI research on different scales, from molecular to processing units [12]. The focus of David Agar in Dortmund is on multifunctional reactors [13]. The research of Andrzej Gorak, also in Dortmund, is directed to the development of separation systems [14]. The team of Adam Harvey in Newcastle does PI research on several subjects, e.g. oscillatory baffled reactors [15].

We observe that PI can be achieved at different scales:

- Fundamental and molecular scale. E.g. by study of the effects of microwaves on molecules and atoms
- Phase and transport scale. Here we can also consider application of the laws of conservation (mass, energy, momentum)
- Equipment and operation
- Process and plant scale – e.g. integration of tasks in one unit

The last two are mainly considered by Lutze in his PhD thesis.

A new, systematic methodology for the application of process intensification was developed at the Computer Aided Process Engineering Center (CAPEC) at DTU in Denmark [5]. This method

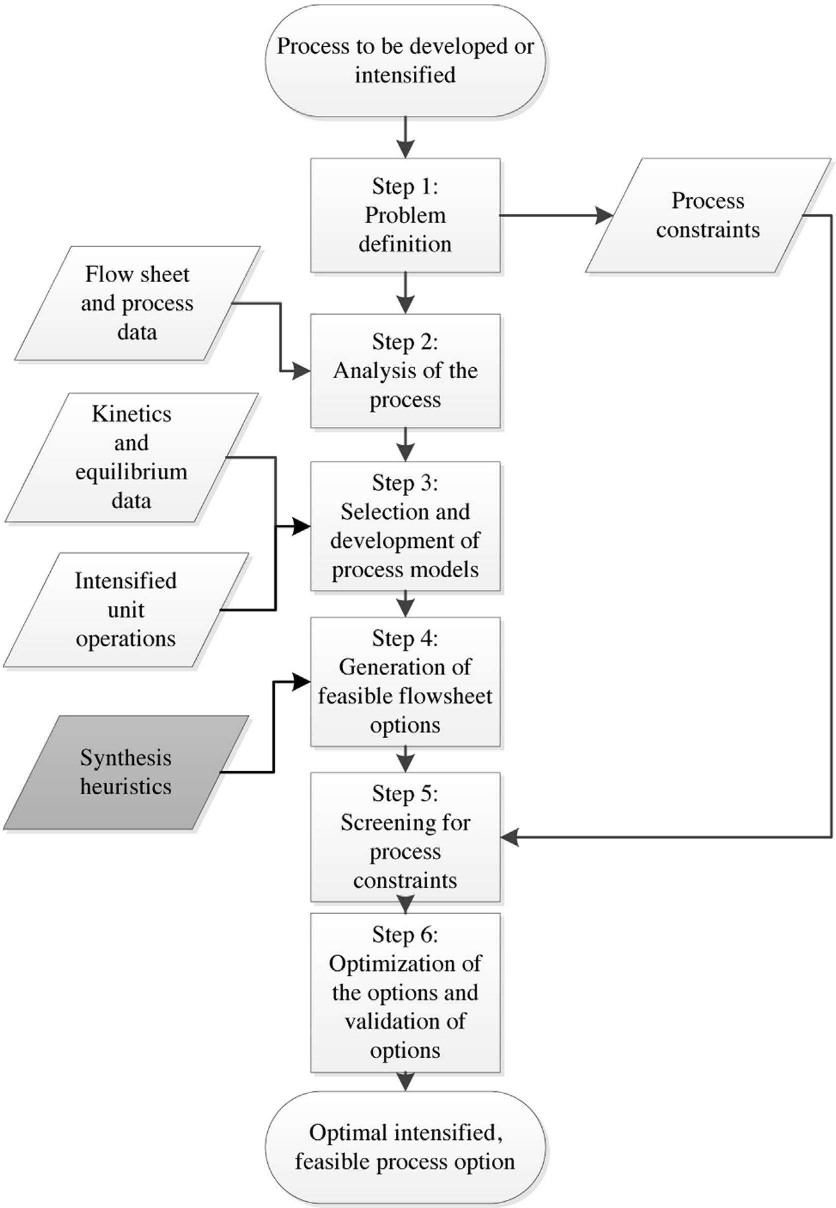

Fig. 1. Schematic representation of PI methodology developed at DTU, with the addition of the use of Synthesis heuristics in the fourth process step (indicated in grey). Steps in the method are indicated with squares, entering data/information is indicated in parallelograms. Adapted from Lutze's thesis [5].

has only been applied to industrially relevant cases from literature, while in this research we apply the method to a running industrial process which was supplied by an industrial partner. Feasibility of the methodology to running processes is crucial for successful implementation, which is the ultimate goal for process intensification methods. For this study, the 4,4′-methylenedianiline (DADPM) process equipped by Huntsman B.V. in the Netherlands is intensified, as Huntsman wanted to gain insight in their process and was prepared to share their industrial data for this research.

The aim of this research is to reduce the total operating costs of the DADPM process, by optimization of material and energy usage in the total process. Detailed process information was obtained and analyzed, and the base case design was thoroughly analyzed for improvement. By the formulation of an objective function (F_{obj}), in the form of Eq. (1), in which Y is a vector of binary decision variables, X is a vector of continuous optimization variables, d is a vector of equipment variables and θ is a vector of product and process specifications, the mathematical framework for the intensification method is set [5].

$$min/maxF_{obj} = \Sigma f_j(Y, X, d, \theta) \quad (1)$$

Together with logical, structural, operational constraints and the process model this will define the optimization of the complete process. These constraints will follow from a user-defined performance metric (PM) in which the most important intensification objectives are collected by the intensification engineer. Depending on the goal of the intensification, this PM can be defined to minimize raw materials, energy costs or recycles for instance. More detailed explanations on this method are given in section two and in the thesis of Lutze [5].

A complete redesign was outside the scope of the industrial partner. This sets the boundaries for the intensification process, but does not hinder the application of the DTU PI methodology.

2. DTU PI methodology for process synthesis and design

The methodology for process intensification used in this research was developed at the Technical University of Denmark (DTU) in the CAPEC-PROCESS group in Department of Chemical and Biochemical Engineering. By analyzing an existing process, limitations and bottlenecks are found and possible intensifications such as combinations of tasks into a single unit operation are proposed. The intensification method yields a large number of possible process options, which are examined based on predefined criteria. The number of options reduces gradually during the execution of all steps in the method until the final and most intensified process option remains. The main methodology workflow is displayed in Fig. 1. In this methodology there are two distinct phases that can be distinguished, there is a clear broadening phase in which all possible process options are generated and considered and there is a phase of selection and narrowing of the options. In short, first the base case design (if existent) is analyzed, using several algorithms. After this, feasible flow sheet options are generated, which are evaluated using several constraints that are formulated in the problem definition. The feasible flow sheets are optimized by calculation of the different criteria that were set for the final design to reduce the number of options to a single one, optimized, option [5,16]. For this research, we have adapted the methodology of DTU. We have extended the early process analysis to generate additional process bottlenecks which are not primarily traced by the DTU method. Additionally, we applied heuristics to concentrate the intensification process on most relevant flow sheet options. This reduces the number of generated options and decreases the effort required for scanning all process options. In the next paragraphs a more detailed description of every intensification step is presented, together with the differences compared to the DTU methodology. For a more detailed description of every step the reader is referred to the PhD-thesis of Philip Lutze and other publications of his research [5,16,17].

In the *first step*, the final goal of the intensification is defined by an objective function, in which a mathematical description of the goal of the intensification method is given. The process scenario (a general description of the desired process) and design scenario (a batch or continuous process) are defined, together with the process and product specifications. The desired maturity of the unit operations used in the intensified process is defined. The maturity is defined as the level of development of the PI unit, for instance only proven on lab-scale (low maturity), pilot plant scale (medium maturity) or already applied in industry (high maturity). A performance metric is defined, containing the important aspects and desired improvements in the intensification, by which the intensified process is judged for its applicability and feasibility. This performance metric is a collection of features of the process (e.g. operational costs, capital costs, equipment size), which should be kept in consideration for the intensification of the process. This performance metric is used for the formulation of logical and structural constraints. Logical constraints are basic constraints based on the functionalities of the desired process, such as ‘a reaction is present’. Structural constraints are limitations to the final flow sheet structure, such as ‘no repetitive units are used’. Based on the product and process specifications, the operational constraints are set. Examples of operational constraints are desired amounts and purity of the product and the energy costs of the process. All constraints need to be satisfied by the final intensified process, and the constraints are used for reduction of the process options. As can be seen from Fig. 2, a Venn diagram containing the three kinds of constraints, different processes obey different constraints, but only the processes that obey all constraints are regarded as feasible by this methodology. The processes that will be accounted as feasible are indicated by an arrow in the figure.

The *second step* comprises of the analysis of the base case design. This is done using mass and energy balances and a base case flow sheet. The base case flow sheet is transformed into a task-based (indicating all tasks that are executed, e.g. reaction, separation) and a phenomena-based (indicating the phenomena taking place, e.g. heating, mixing) flow sheet using different algorithms as are described in the original method [5]. In these algorithms, a stepwise identification of tasks is obtained by applying general rules of identification of tasks and calculations

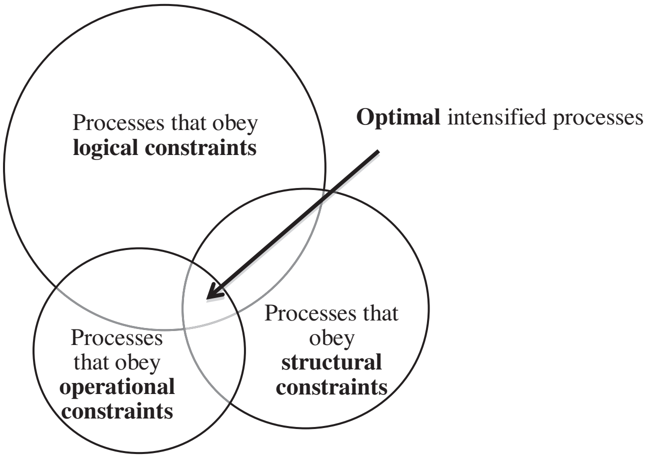

Fig. 2. Venn diagram representing processes obeying different constraints. Feasible results are indicated by the arrow, and present in the region where all constraints are obeyed.

are done based on the objective function and the contribution of the separate unit operations is calculated. Unit operations and process functions such as heating or cooling that have a large negative influence on the objective function are identified. The cause for these limitations is identified by analyzing pure component properties, mixture properties and reaction properties using algorithms from the DTU method [5]. Sub-problems in the process intensification are identified by dividing the process in sub-processes that do not influence each other, also using a simple algorithm. Instead of intensifying the process as a whole, these sub-problems allow for a section-wise approach of the problem. At this point, all information on the base case is analyzed and the limitations are known. Next, PI equipment is collected using a knowledge base search. For this search, a good and up-to-date knowledge base is required, which contains detailed information on all process equipment available. In the knowledge base all PI equipment available to date is described by its technical data, e.g. operation window, suitable phases and maturity. PI equipment that is found is pre-screened on their potential applications in the process by comparing the necessary process conditions to the operating frame of the PI apparatus. Equipment that is not suitable is removed from the search space, reducing the total number of process options. In the first and second step the DTU method concentrates on the objective function, unit operations, equipment and constraints. Process synthesis aspects get less attention.

In the *third step*, models are developed for all possible **PI equipment** that was found in the previous step. For these models, descriptions and experimental results are desired, but not all of them are available in literature reducing the reliability of the models and making a comparison difficult. In this research, the models are made using Aspen Plus, and all models generate output on mass and heat efficiency, resulting in the ability to do cost calculations on the process. In all models the overall efficiency and performance data are used, some in a black-box approach and some in a more detailed approach, depending on the information that is available on the PI equipment. Where possible, detailed Aspen models have been developed. In a number of cases we had to develop Excel models and implement these in Aspen.

The *fourth step* is the generation of feasible **flow sheet options**. In the DTU method a superstructure approach is used. In this step, all models are linked in all possible ways and using all possible recycles to obtain a large amount (defined as NPO: Number of Process Options) of potential process options. From this point, the method is focusing on the reduction of flow sheet options. All generated options are screened by logical and structural constraints, resulting in a substantial reduction of process options. For this research, this step is altered from the DTU methodology and heuristic rules for process design (e.g. from Barnicki [18]) will be incorporated in the generation of feasible process options. This is done by removing manually flowsheet structures violating the heuristics. Such heuristics are for example: do not put a separation before a mixing, or do not cool before heating. This relates to the determination of process sequences and connections, not to the PI equipment applied. If in the implementing of heuristics uncertainties arise about intensified process options, these options are kept as a possible to avoid incorrect rejection. By adding the heuristic input, the least attractive options will be removed in an early stage of the intensification process, leaving more room for focusing on essential differences between more attractive process options. The use of heuristics will result in significantly less process options. This reduces the number of models that has to be made and evaluated, reduces calculation time required in the selection and optimization step, and concentrates our effort on the development of most relevant process options. The addition applied combines process engineering know how and a mathematical approach of optimization.

In the *fifth step*, the models that are generated in the third step are used for scanning the process options on the operational constraints. With the remaining process options after step 4, the models are incorporated to full processes which are screened based on their performance in reference to the objective function. All remaining process options are modeled using ‘short-cut’ models (including literature data on material transport, energy efficiency and kinetics). These short-cut models are built using Excel, which is linked to Aspen Plus to be able to model unit operations not present in the Aspen library. The processes that obey the operational constraints are kept in the list of feasible intensified processes. To further reduce the options, all processes are screened by evaluating the performance metric and objective function and the least feasible options are discarded. The performance metric and objective function may consist of cost indicators, but also for example the energy usage, equipment usage and waste production.

The *sixth, final step* comprises of solving the reduced optimization problem and identification of the single, optimized option. This is done by more detailed modeling of the remaining options in one flow sheet (see Section 3.4) and the optimization of the processes by optimizing the objective function using Aspen Plus. Validation of the optimized process is done using rigorous simulation of this single process. In this step, the objective function plays the decisive role on the identification of the best process option.

3. Application to the Huntsman DADPM process

Application of the DTU method application to a running process with an industrial partner might yield additional information on the applicability of the method. Therefore, in this research the data of a running process were used for optimization. The process at hand is the 4,4′-methylenedianiline (DADPM) process, running at Huntsman B.V. in Rotterdam, the Netherlands. This process is part of the Methylene diphenyl diisocyanate (MDI) process in the polyurethane industry.

3.1. Step 1: problem definition

DADPM is produced by the acid catalyzed condensation of aniline with formaldehyde. The main reaction that is taking place is the acid catalyzed reaction of formaldehyde with aniline, as shown in Eq. (2). Side reactions are not defined for the intensification, assuming that after isomerization all formaldehyde has been converted into the desired products. Acid is neutralized by sodium hydroxide via the reaction shown in Eq. (3). The purity of the DADPM produced depends on the ratios of aniline, formaldehyde and catalyst used and reaction time and temperatures.

$$2C_6H_5NH_2 + H_2CO \xrightarrow{HCl} DADPM + H_2O \tag{2}$$

$$HCl + NaOH \rightarrow NaCl + H_2O \tag{3}$$

A simplified block diagram of the process equipped at Huntsman is shown in Fig. 3. At Huntsman (and in other commercial processes described in literature [19]) aniline is premixed with the acid catalyst, usually hydrochloric acid. Excess aniline is used in this process. Formaldehyde (contaminated with traces of methanol) is fed to the reaction mixture in multiple stages to increase temperature control and thus yield more favorable reaction products. The reaction mixture is transferred into three reactors until all formaldehyde fed has reacted. After the completion of the reaction the reaction mixture is fed to an isomerization section in which two isomerization towers are used.

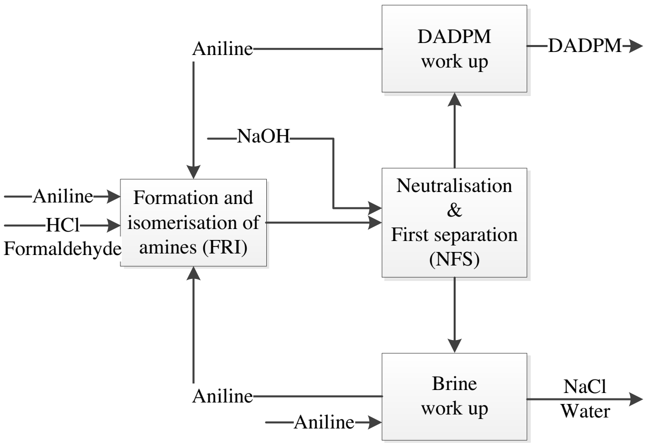

Fig. 3. Task-based flow sheet of the DADPM process.

After the isomerization the mixture is neutralized using aqueous sodium hydroxide, in which water and salts are formed. After the neutralization, the organic phase is separated from the water phase for further purification of both phases. The organic phase, containing most of the DADPM produced is contaminated with brine, aniline and water which should be separated for the purification of DADPM. The aqueous phase is worked up in another section of the process, in order to remove all organics and other contaminations from this section.

Both detailed mass and energy balances (Aspen simulations based on operation data) were available for this research. As the process is complex (many operations and recycle streams, e.g. fresh aniline to Brine work up for wash and used aniline + other components to FRI) and the aim of this research is to analyze the methodology, the decision was made to not intensify the entire process, but to focus on two sub-sections of the process. One of these sections is analyzed by the extended DTU methodology while the other is optimized using a more heuristic process design approach.

The objective function that is defined for this intensification is the minimization of the operational costs, which includes the costs of raw material, energy and make-up costs, and is mathematically represented by Eq. (4). As capital costs were not in the objective function (in agreement with Huntsman), the costs of the retrofit are not considered in the intensification of the process. The process scenario will be close to the existing process, as reactants are not to be altered in the intensification. The design scenario is a continuous process.

$$\min F_{obj} = \left(\sum c_{RawMat,i}\dot{m}_{RawMat,i} + \sum c_{energy,i}\dot{E}_i + \sum c_{solvent,i}\dot{m}_i\right)/\dot{m}_{DADPM} \quad (4)$$

The process and product specifications are taken from the base case design, which are summarized in Table 1.

Generally speaking, the performance metric for this intensification analysis is defined as: energy efficiency, energy consumption, operating costs and simplification of the flowsheet (e.g. reduction of number of unit operations) and capital costs. This performance metric is used for identification of constraints which the intensified process should obey. Examples of these constraints are given for the brine work-up section in Table 2. Huntsman first of all wanted to improve the performance of the existing plant (less energy and operational cost) before considering equipment modifications. All categories of intensified equipment (from low to highly mature) can be used in the intensified process.

3.2. Step 2: analysis of the process and proposed intensification approaches

Based on the complete flow sheet (not available for publication) an analysis of the DADPM process is done. The process is divided in the four sections represented in Fig. 3, as these are identified as the sub-processes according to the methodology. The separate sections contain several unit operations and internal recycles of material and energy, which all contribute to the objective function. All these sections are analyzed based on the steps in the methodology and their base case design. In this analysis, the contribution of the different unit operations and sections to the objective function are calculated. Task and phenomena based flow sheets are produced for all sections and the objective function is calculated for all tasks in the process, together with the identification of other limitations and bottlenecks. An example of such a task-based flow sheet (for the brine work-up section) is shown in Fig. 4. This task-based flow sheet is transferred into a phenomena based flow sheet using the translation of tasks into phenomena as can be seen from Table 3.

Using the task and phenomena based flow sheets the possible limitations and bottlenecks of the process are identified by the analysis of pure component, mixture and reaction properties. Furthermore, a knowledge base search using the DTU knowledge base and additional sources is done to identify known limitations of the different unit equipment that is used in the base case design.

Material costs account for the largest contribution to the operational costs (as can be seen from Fig. 5), but as the material efficiency of the process is already ~100% it is difficult to reduce the operational costs by reducing material costs. Therefore, only the contribution of the energy costs to the objective function is taken into account for deciding on the section to be intensified.

The total energy costs are in the order of ~1 M€/year, which might be reduced by intensifying the process. If material costs would be considered in the remainder of the intensification, the relative reduction on the objective function would be minor. We could have avoided the investigation of materials and their contributions to the objective function if they were not present in the objective function.

From Fig. 5 it can be seen that the brine work-up section has the largest contribution to the energy costs and therefore this section

Table 1
Specifications of raw materials and products for intensification of the DADPM process.

Raw materials	Specifications
Aniline	liquid, 1000 ppm benzene, 1000 ppm nitrobenzene
Formaldehyde	liquid solution, 47 wt% CH_2O, 0.50 wt% MeOH, 52.50 wt% water
Hydrochloric acid	aqueous solution, 30 wt% HCl
Sodium hydroxide	liquid solution 50 wt% NaOH, 50 wt% water
Products	**Specifications**
DADPM	99.9 wt% purity, >29000 kg/h

Table 2
Constraints found for the brine work-up section.

Logical constraints	No reaction is present
	The outlet of methanol should be connected to a purification unit
	The outlet of aniline should be connected to a purification unit
	The outlet of water should be connected to a purification unit
	Do not exceed the number of units of the base case design
Structural constraints	
Simplification	Do not use pre-reactors
	Do not use repetitive units
	Do not use enrichments before separations if not necessary
Efficiency	Do not integrate units which inhibit each others' performance
	Add units in the flow sheet in which it has the highest efficiency
Energy	Do not connect units with alternating heat addition and heat removal
Operational costs	Make sure that in the flow sheet units are connected to ensure the high efficiency of the raw material usage and/or which allow the recycle of raw materials
Operational constraints	
General	At least 100 kg/h of methanol with a purity of 75 wt% should be exerted
	The purity of the aniline sent to the feed section should be at least 90 wt%
	The purity of the water sent to the DADPM work-up section should be at least 95 wt%
	All salts should be exerted in this section
Energy	Do not use more energy than the base-case design
	Do not exceed the heat supply used in the base-case design
Operational costs	Raw material consumption should not exceed the base case design usage
	Efficiency should be increased compared to the base case design efficiency
	Utility costs should not increase compared to the base case design
Capital costs	Keep the volume as low as possible

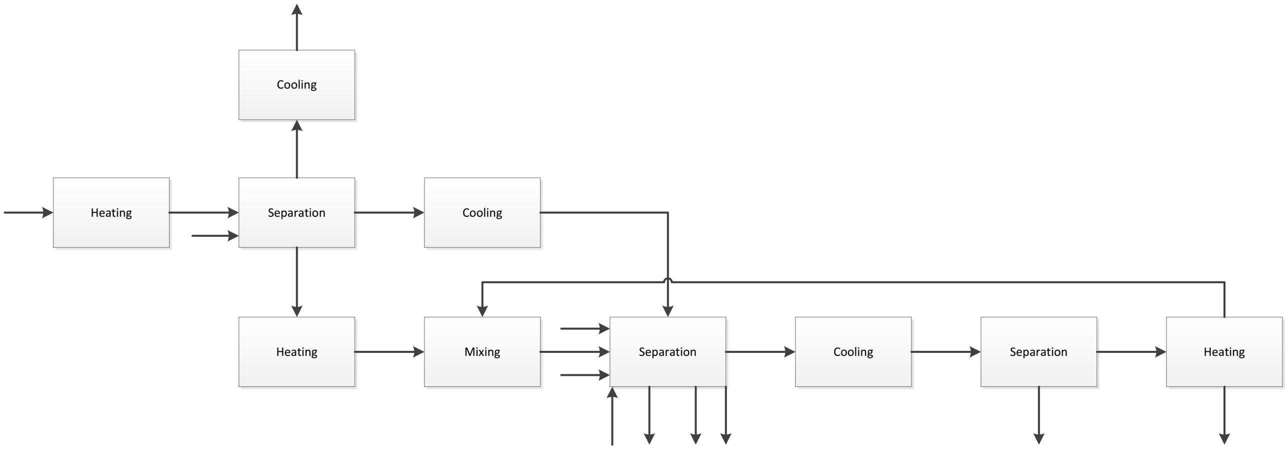

Fig. 4. Task-based flow sheet of the brine work-up section of the DADPM process.

Table 3
Identification of the different phenomena in the brine work-up section.

Task	Important phenomena
Heating	Mixing, heating/cooling, (phase transition V-L, phase transition G-L, phase separation)
Separation	Mixing, heating/cooling, phase transition, phase separation
Cooling	Mixing, heating/cooling, (phase transition V-L, phase transition G-L, phase separation)
Mixing	Mixing phenomena, (phase transition L-L, phase separation, heating/cooling)

will be intensified in the remainder of the research. Also, it can be seen that the neutralization and first separation have little direct energy costs, yielding that it would not be the first choice of intensification by the DTU methodology. However, as we find that the first separation has a large influence on both the brine and DADPM work-up sections and this first separation has a relatively low efficiency in the current process, this section is interesting for intensification. The unit operation currently operated is fairly simple, but yields bad separation specifications, yielding a large influence on both brine and DADPM work-up sections, which is an indication that it might be a bottleneck. The DTU methodology does not indicate this separation as a bottleneck as it does not directly contribute largely to the objective function, but indirectly it might have a large influence on the costs of both the brine and DADPM work-up sections. To be able to compare the intensification method with heuristic design approaches and as this section was

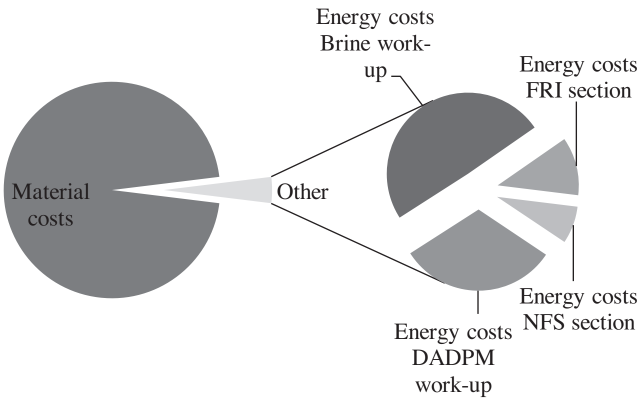

Fig. 5. Contribution of different sections to the energy costs and the contribution of the energy costs on the total operating costs.

not identified by the DTU methodology, this section will be intensified using a heuristic process design approach. The approach of intensification is as following:

- Intensification of the brine work-up section according to PI methodology
- Intensification of the neutralization and first separation using heuristic process design

3.2.1. Intensification approach of the NFS section

The NFS section is intensified using a general process design approach, following the steps shown in Fig. 6. In this approach the intensification is done based on the comparison of ideal behavior and actual plant data. There are three distinct phases in each process design. In the first phase, the scope and design basis for the new process are defined and a first literature search is conducted to gain information on the process. A process overall approach and conceptual design with alternatives are made at the end of phase one. The second phase consists of the evaluation of the possible process designs. For the selected design a mass balance will be composed, together with a process flow sheet. The third phase starts with a process flow diagram and the detailed design of the equipment used in the process. After this design the safety and economical aspects are evaluated. In this project, the main aim is to intensify the process. After the conduction of the mass balances of the intensified process and the selection of equipment to be used the process is considered intensified. Before the actual process can be built all equipment should be designed in more detail, but this is out of the scope of this project. Therefore, in the intensification of the NFS section, only phase one and two of the design approach will be followed.

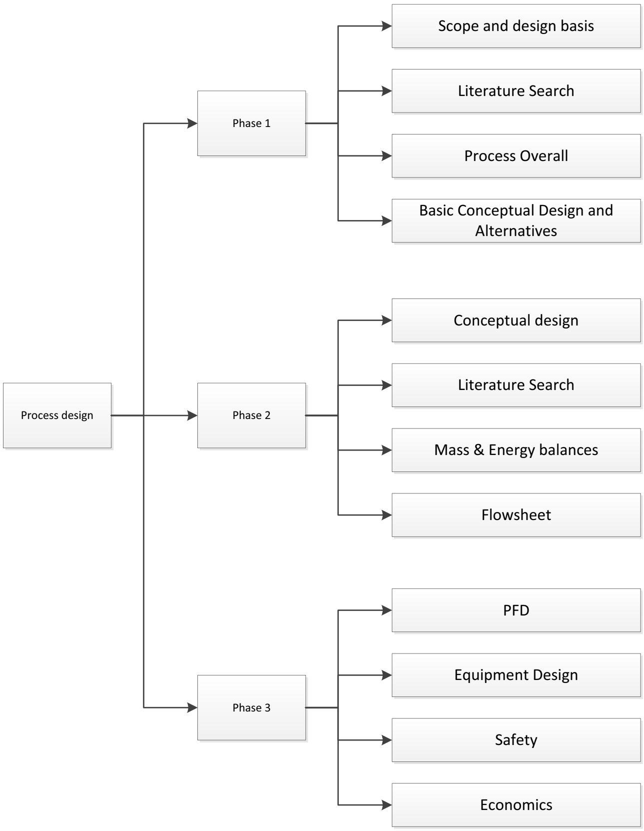

Fig. 6. Approach for the intensification of the NFS section, done using conventional process design methods.

The critical analysis and redesign of the NFS section based on first principles of solubilities and fluid properties, has led to an improved performance of the NFS section. The poor operation of the NFS section was not traced by the DTU method, as the operational costs of the separation are low. The intensified NFS section also provided less polluted feeds to the Brine work-up and DADPM sections.

3.2.2. Intensification approach of the brine work-up section

For the intensification of the *brine work-up section* the DTU methodology will be followed, depicted in Fig. 7. On the left hand side of this figure the approach that is used in the DTU methodology is shown. As this approach yields a large amount of PI options that should be examined one-by-one, the methodology is slightly altered for this project. The altered method is shown on the right hand side.

3.3. Step 3: selection and development of process models

For the altered methodology potential PI equipment is selected in step U2. This is done by doing a knowledge base search based on the analysis of the process. The found process equipment is prescreened by comparing the operating range of the apparatus with the desired range in the intensified process. After this the most promising PI equipment is selected in step U3. To this end, a literature search is conducted on all PI equipment found in step U2. The goal is to identify two or three equipment options per task by evaluation of the applicability of the PI equipment on the specific task, based on reported efficiency of application in literature. This selection drastically reduces the amount of possible processes that should be examined. This is different from the DTU method, in which all identified PI equipment should be modeled in step U3 for the generation of superstructures in step U4. For the brine section, there are four separations indicated of which three yield intensification options after step U2. The first separation could be intensified using either an agitated cell extractor or a centrifugal extractor, the third separation could be intensified with a heat integrated distillation or an adsorption distillation, while the fourth separation could possibly be improved using a centrifugal phase separator or a packed vessel.

3.4. Step 4: generation of feasible flowsheet options

In step U4 of the altered method the number of process options is evaluated and all process options are generated. Only the best process options are reviewed in the altered method, instead of all options. To this end, heuristics are applied for the generation of the feasible flow sheet options [18]. No superstructure in which all

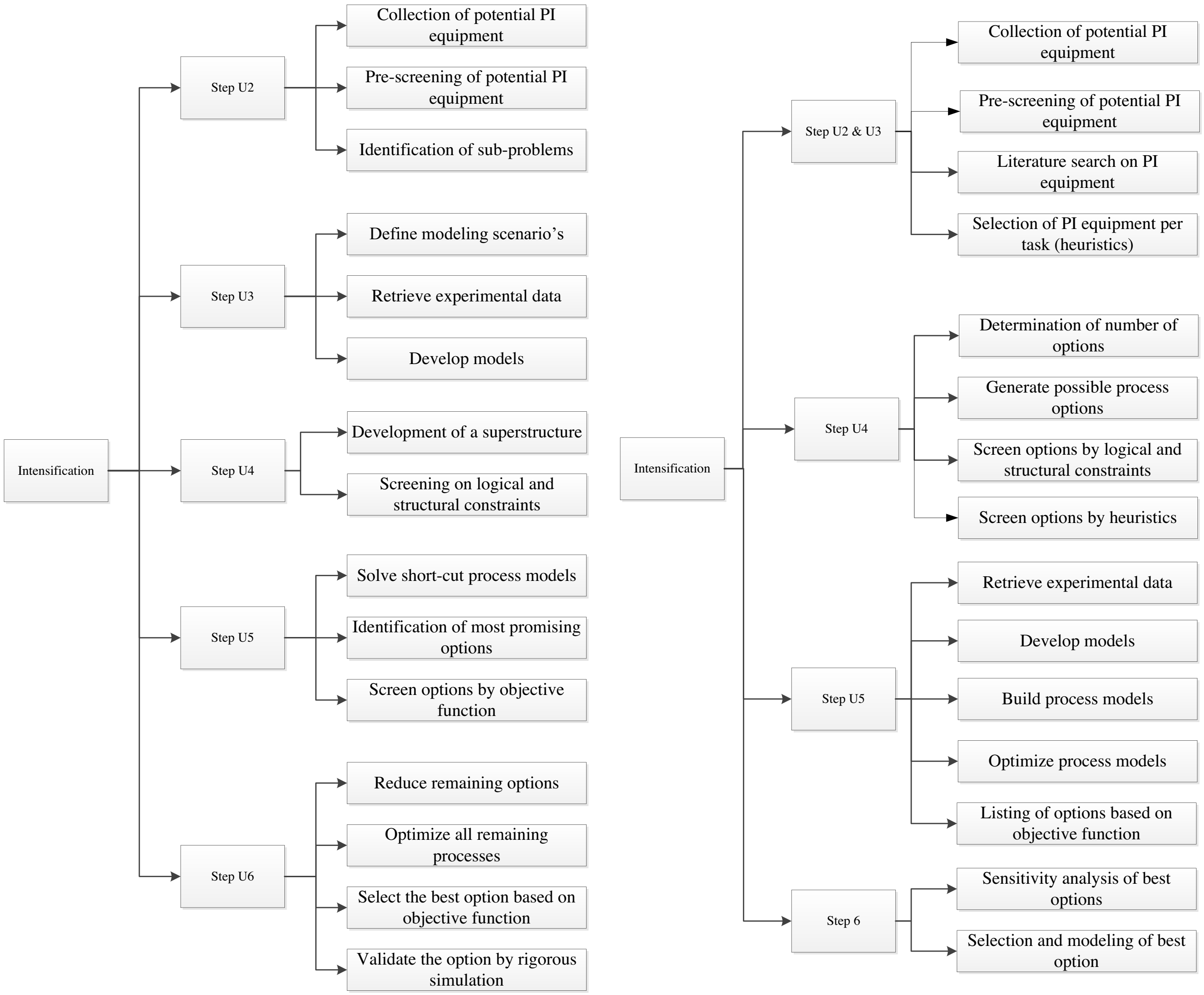

Fig. 7. Project organization for PI method approach, left the original unit operation (U) based DTU method [5], right the adjusted method applied in this project. Important adjustments are the addition of heuristics in the selection of feasible PI equipment and in process options (Step U3 and U4) and the sensitivity analysis of best options (Step 6). Apart from that, the sequence of the steps to be executed is altered, so that models are not built before they are required.

possible process options are represented is developed in detail as was done in the DTU method [5]. Not using a superstructure reduces the amount of process options that are evaluated, reducing the calculation time for optimization. A drawback of this adjustment is that not all options are modeled and thus not all options are quantified, however by application of heuristics in a proper way, this would not result in the overlooking of the optimal process option. When applying the rules, the amount of options is reduced, e.g. by the rule ‘separate big streams earliest’, several process options that separate small impurities before making large separations are ruled out. Other ‘rules’ are for example that the hardest separation should be done last, as well as high purity separations. These heuristic rules can be included in the structural constraints in the DTU methodology, to reduce the amount of process options that need to be computed. For the intensification of the brine section there are ten identified tasks, which will yield a large amount of process options (2^{10}–3^{10}), even when only two or three types of equipment are selected per task. Therefore it is decided to first reduce the task-based flow sheet to the four indicated separation tasks as the mixing and heating tasks are subordinate to the separation tasks that have to be executed. The mixing and heating the tasks are only used to yield the desired inlet and outlet streams for the separations and waste streams, which might not be necessary if the separations are performed by different types of equipment. Therefore it is justified to reduce the number of tasks in this part of the process to the four separation tasks, which are listed in Fig. 8. If for all of these separation tasks three PI operations are selected and the base case is considered, the number of process options (NPO) can be calculated by the equation below. In this equation, NIU is ten (for the Number of Identified Units, see Fig. 4) and ps (Process Steps) is four, as there were four tasks identified, which yields a total of 18.6×10^4 options. This number of options is represented by a generic superstructure as was shown in the methodology of DTU [5].

$$NPO = \sum_{ps=2}^{4}\left(NIU^{ps} * 2\sum_{2}^{ps}(ps-1)!\right) = 18.6 \times 10^4 \qquad (5)$$

3.5. Step 5: screening for process constraints

To model 18.6×10^4 process options will still yield too many variables to be able to justify any selection that is made. Therefore, some heuristic rules obtained from Barnicki and Fair [20,21]

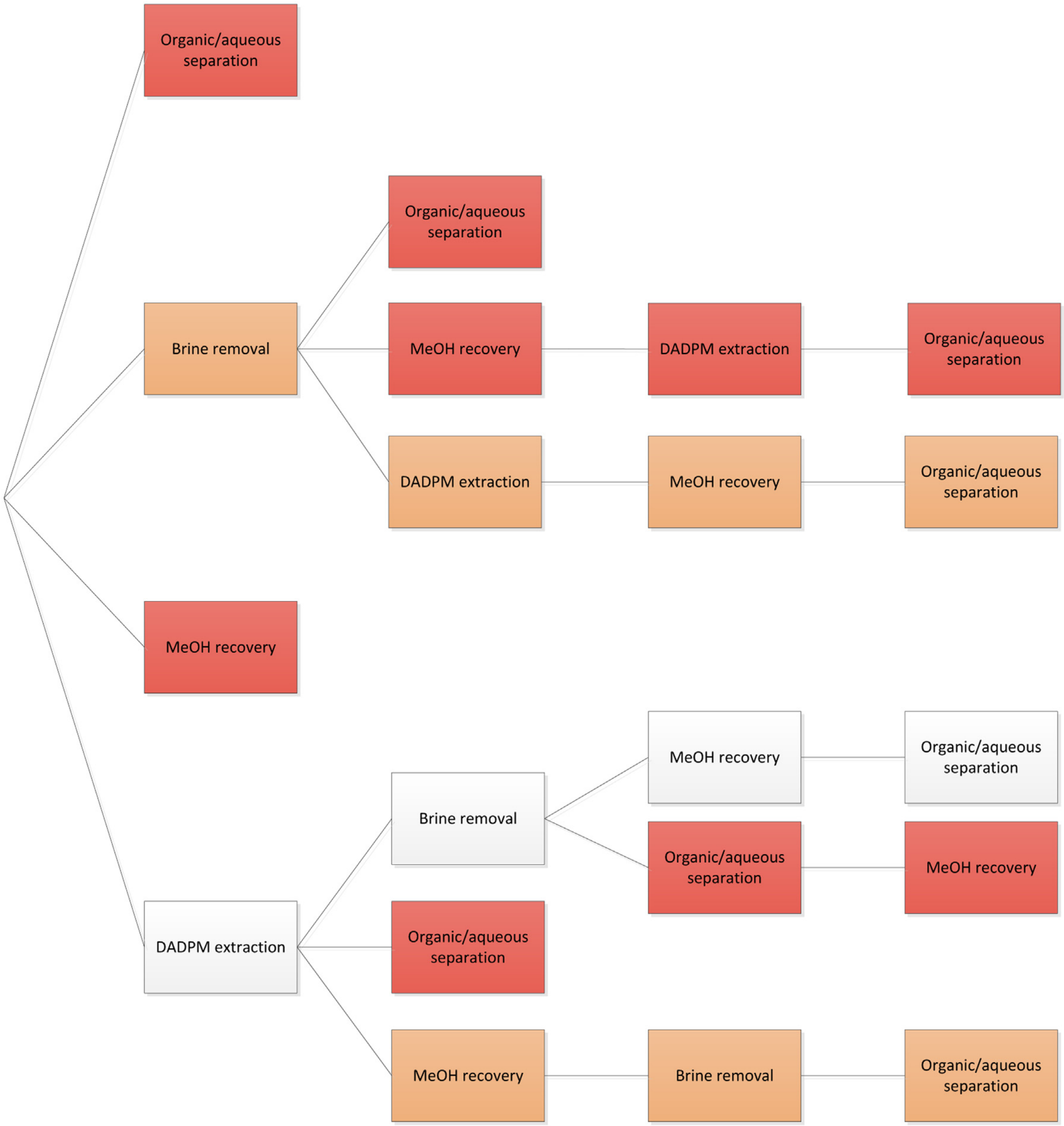

Fig. 8. Selection of promising task-based options for the brine work-up section using Barnicki's rules for process design. Routes in red are discarded as not effective, orange routes are considered with limitations and the white route is the preferred route. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

regarding the design of process separations will be applied to identify the possible process routes. The rules that are supplied by Barnicki and Fair enhance the ability to compare different options on a physical and realistic basis, and allow the engineer to consider different options without having to do a rigorous mathematical optimization. By applying heuristic rules the engineer has the

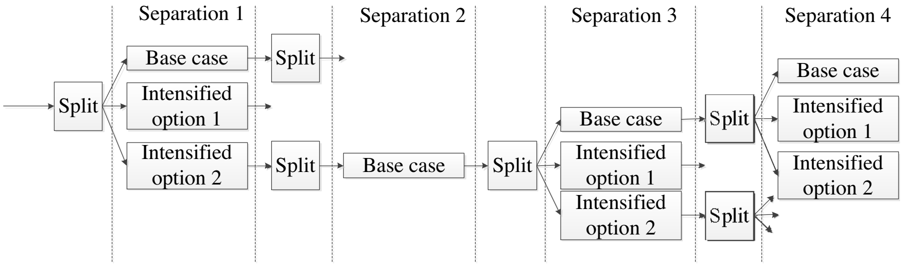

Fig. 9. Tree-structure approach of process modeling in Aspen Plus. For every process step, all identified options are modeled including the base case obtained from Huntsman, with a split in front. This split can be varied so that bigger streams will go to different unit operations. Based on the cost calculation for every option, the best process option can be identified in this way.

influence on which factors should play a significant role in the intensification of a process (e.g. avoiding recycle streams) and the overview of all process options becomes clearer. In other words, this approach of PI allows engineers to consider and make choices based on knowledge instead of calculation force only. Heuristics applied in this intensification are; reducing the separation load, to remove corrosive and unstable components as early as possible, do the most difficult separation last and do high purity separations in the last step. Also, the addition of new components is avoided. For the brine section, this application of these heuristic rules leads to the conclusion as illustrated in Fig. 8. The process routes drawn in the red streams are discarded immediately, while the white process route is indicated as most promising from the rules of Barnicki and Fair.

After the selection of the most promising routes the process models can be made, which is done in step U4, U5 and U6. For the selected PI equipment models are developed based on experimental data or assumptions for missing data items. The models are developed in Aspen Plus V7.3, which facilitates the connection of the models into a flow sheet. Existing models can be altered or completed using external tools such as Microsoft Excel. In Aspen, there is the possibility to add external models for equipment that is not defined by Aspen or to enhance the level of modeling for existing equipment through a Calculator Block. Usage of these Calculator Blocks gives rise to the opportunity to add extra calculations to Aspen and return the values calculated in Excel for further usage in Aspen. Process and flow conditions can be exported to Microsoft Excel (including an Aspen add-in), in which the model is built, and the result of this model is imported back into Aspen for continuing calculations on the flow sheet. In Excel, all its normal functionalities can be used, so models can be built with any desired level of detail. The generated options are manually screened for the logical and structural constraints as well as the total objective function. The remaining options are shown in Fig. 9.

Summarizing, the narrowing of options is done in four steps: first generation of flowsheet options using heuristics, next reduction of the Number of Identified Units, third systematic generation of superstructures for NIU and Process Steps (ps), fourth elimination of superstructure options by means of synthesis heuristics and modelling.

3.6. Step 6: optimization and validation of the process options

In the final step a global sensitivity analysis on the models is done to identify the single best process option. This sensitivity analysis is an addition to the original DTU method and is done by building a general calculation structure in which all remaining options are present (as shown in Fig. 9) in Aspen Plus and afterwards optimizing the process by varying the splits between all process steps towards the different options. For every task, the options are modeled parallel with a split before them. An optimization step based on the costs of the entire process will be done to determine the most favorable option by adjusting the split factor before every task in Aspen. This sensitivity analysis will yield results for all process options, in which the total costs for all options are calculated and thus the best one can be identified. In total, 27 process options are modeled in this tree-like structure including 13 splits (one before separation 1, three before separation 3 and nine before separation 4, as indicated in Fig. 9). This means that an analysis with 26 variables (two per split into three streams) should be done to identify the best process option. In this sensitivity analysis all splits are varied from 0 to 100 percent into all streams to calculate the influence on the total operating costs for the process. Aspen is able to optimize these streams in such a way that the minimal total operational costs are obtained by sending the largest stream in the most feasible process option. In contrast to the methodology from DTU the process options are directly compared on the same level by this optimization to find the optimal intensified process. Before choosing the optimized option, all remaining options are screened on the same criteria, yielding a better comparison and will lead to a better final decision on the best process option, with a smaller chance of sub-optimization of the process.

3.7. Results

Intensification of the Neutralization and First separation (NFS) is done by approaching the theoretical equilibrium in the process to a greater extent, which can be obtained by intensification of the existing equipment. For this intensification assumptions on both phase and thermodynamic equilibrium are made, and experimental data of the equilibrium in the DADPM system was used. The distribution of salts in both the organic and aqueous layer is enhanced towards a more favorable situation. This intensification was done applying heuristics and general knowledge of process engineering, instead of using the method developed by Lutze [5]. As a result of this intensification the costs of both the DADPM and brine work-up sections are reduced substantially, as can be seen from Table 4. If only the original method would have been used, this would not have been indicated as possible intensification. These costs were calculated using a flowsheeter and altering the inlet of both sections as a result of the intensified separation between the aqueous and organic phase in the NFS. The energy costs of the DADPM work-up section can be reduced by 11% and the energy costs of the brine work-up section are even reduced by 18%, only by intensification of the first separation, as was calculated from the altered model.

The intensification of the brine work-up section was done using the altered Lutze methodology and a flowsheeter for finding the optimum intensified option. By adjusting the splits as shown in Fig. 9, the optimal process was found based on mass and energy data and comparing all process options using a sensitivity analysis. This sensitivity analysis is an important addition to the original method, as in this way all possible processes are compared on the same level for feasibility. The objective function for minimization of the operational costs is satisfied by the found intensified process for the brine work-up section. This process is schematically drawn in Fig. 10. Two separations have been intensified, for two other separations the base case design was found to be the best option. Separation three can be enhanced by heat integrated distillation, while separation four yielded a packed vessel as the most feasible option.

The reduction of the total costs as a result of this intensification is 5% as is shown in Table 5. The total reduction in energy costs of the brine work-up section if both the first separation and brine

Table 4
Indexed energy costs for work-up sections after intensification of NFS section.

First separation scenario	DADPM section (indexed costs)	Brine section (indexed costs)
Base case NFS	100	100
Intensified NFS	89	82

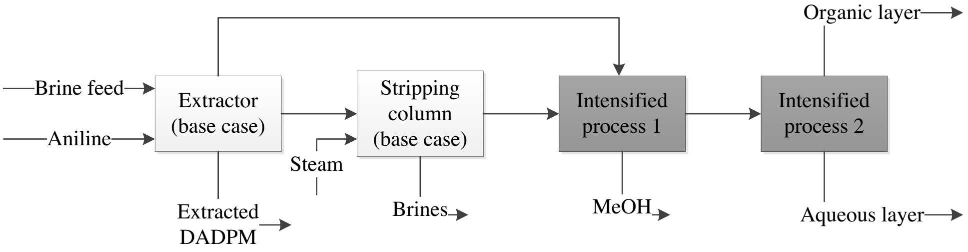

Fig. 10. Simplified intensified process option for brine work-up section with two intensified tasks.

Table 5
Indexed costs for brine work-up section after intensification of different sections.

Design	Indexed costs
Brine base case	100
Brine intensified, base case NFS	95
Brine intensified, intensified NFS	76

work-up section are intensified is 24%, which is a significant reduction. This will yield a reduction in costs of ~0.25 M€/year.

4. Discussion and conclusion

The DTU methodology is straightforward and structured, which results in a clear workflow in which it is hard to miss any details. It is valuable to work in a structured way, but some of the algorithms are lengthy and devious for a trained chemical engineer. The definition of the objective function is done in the first step of the methodology, where no information on the process is known. This might result in a mismatch between the objective function and the process, as is the case in this research where the objective function was unsuitable due to a high base value of material costs and a material efficiency of ~100%. A feedback within the intensification methodology would result in a more appropriate objective function. A pre-screening of the base case process based on heuristics would result in more knowledge and the ability to select a better-suited objective function for which the optimization would yield bigger relative reduction, and a better distinction could be made between the different intensified options. Apart from that, a better defined objective function reduces the work-load in the methodology, as the analysis of process limitations and bottlenecks is focused more on the parts of the process that can actually be improved.

In general it can be said that the methodology could be more homogeneous to benefit the overall process intensification. At the first part of the method it focuses on identifying the tasks necessary, but in the intensification part the focus is shifted towards the unit-operations, in either the unit operation or the phenomena based workflow. Input of the user is determining the homogeneity of the method, which is undesirable as it might differ the final results of the intensification. Focus on tasks is desirable as this might yield new and creative alternatives for the process, while the focus on unit operations reduces this creativity. For the focus on tasks it is beneficial to analyze the process in more detail than is done in the current approach, and that the reasons for limitations are used in the intensification.

Without models available, the modeling of all PI options is a large amount of work. Pre-screening of the options is based on information in the knowledge base, which is only sufficient if the knowledge base is complete and up-to-date. An additional screening based on literature is valuable for the identification of the most promising alternative equipment per task and reduction of the work-load. Focusing on tasks instead of equipment would yield larger improvements and is a more innovative approach.

The decision for the best process is done based on quantitative arguments, while the errors in the calculations and models are not taken into account. It would be very valuable to add a sensitivity and error analysis to the intensification methodology in which the calculation errors in the models are taken into account. The method is based on improvements on unit operation level, while in a more heuristic approach the general process design (the sequence of unit operations etc.) is more important. Interconnection and interplay between different unit operations is of high importance in process engineering, and optimizing of single unit operations might yield to a sub-optimization of the total process.

For this research, the methodology was slightly altered, which resulted in better selection of process options. In the altered method there are selection steps based on heuristics and general process engineering rules earlier in the intensification process. In the original method only mathematical selections are done for the selection of the best process, resulting in the possibility of overlooking the best option and missing crucial process information.

A sensitivity analysis (by testing different specifications in the intensified process options) on the identification of the final intensified process is desirable, as with this information the decision on the final process can be made with more confidence. This sensitivity analysis can be added in the final step of the DTU methodology.

Application of the methodology on the DADPM process did not yield large improvements on the objective function. In the objective function that was used for this research (minimization of operational costs), the main contribution are the material costs. However, as the material efficiency was ~100%, there was no reduction possible in this cost. As a result, only variables which have a marginal effect on the objective function were optimized, yielding a small result in the total objective function. The reduction of the energy costs after the intensification was substantially, which indicates that this intensification was useful. If minimization of energy costs would have been defined as the goal of this intensification the application of the PI method would have resulted in a significant reduction of the objective function. The biggest improvement on the DADPM process was obtained by enhancing a task that was not identified as a limitation in the analysis using the DTU method. We have shown how the improvement of a specific section which is linked to two additional sections can create improved performances in the connected sections. These tracing of the root cause of mal-operation was done by engineering practice and is not included in the DTU method. A more detailed or engineering based analysis of the process can be done to identify more important limitations. Comparison of real-time data with the design specifications could yield insight on equipment that is not operating properly.

In conclusion, it can be said that the methodology is very useful and can help to find limitations and bottlenecks of a process, but that user input is of great importance for the result. The knowledge base is a great tool, but it should be updated regularly and additional information is required for a well-informed decision. It is not possible to exclude any user-input and heuristics in finding the best possible process option. Process synthesis based on heuristics should be a substantial part of the method for optimizing the total process instead of focusing on unit-operations.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

References

[1] A.I. Stankiewicz, J.A. Moulijn, Process intensification: transforming chemical engineering, Chem. Eng. Prog. 96 (1) (2000) 22–34.
[2] C.P. Tsouris, V. Joseph, Process intensification—has its time finally come? Chem. Eng. Prog. (October) (2003).
[3] T. Van Gerven, A. Stankiewicz, Structure, energy, synergy, time—the fundamentals of process intensification, Ind. Eng. Chem. Res. 48 (5) (2009) 2465–2474.
[4] C. Ramshaw, Higee distillation—an example of process intensification, Chem. Eng.—London 1983 (389) (2016) 13–14.
[5] P. Lutze, J. Woodley, R. Gani, An Innovative Synthesis Methodology for Process Intensification, DTU Chemical Engineering, 2011.
[6] W.T. Cross, C. Ramshaw, Process intensification—Laminar-flow heat-transfer, Chem. Eng. Res. Des. 64 (4) (1986) 293–301.
[7] S. Becht, et al., An industrial view of process intensification, Chem. Eng. Process. Process Intensif. 48 (1) (2009) 329–332.
[8] J.A. Moulijn, et al., Process intensification and process systems engineering: a friendly symbiosis, Comput. Chem. Eng. 32 (1–2) (2008) 3–11.
[9] A. Pohar, I. Plazl, Process intensification through microreactor application, Chem. Biochem. Eng. Q. 23 (4) (2009) 537–544.
[10] C.R. Strauss, R.W. Trainor, Developments in microwave-Assisted organic chemistry, Aust. J. Chem. 48 (10) (1995) 1665–1692.
[11] I.S. Franssen, et al., Practical challenges in the energy-based control of molecular transformations in chemical reactors, AIChE J. 60 (10) (2014) 3392–3405.
[12] B. Gielen, et al., Characterization of stable and transient cavitation bubbles in a milliflow reactor using a multibubble sonoluminescence quenching technique, Ultrason. Sonochem. 25 (2015) 31–39.
[13] A.-K. Liedtke, et al., Liquid–solid mass transfer for microchannel suspension catalysis in gas–liquid and liquid–liquid segmented flow, Ind. Eng. Chem. Res. 54 (17) (2015) 4699–4708.
[14] T. Färber, et al., Different recycling concepts in the homogeneously catalysed synthesis of terpenyl amines, Chem. Eng. Process. Process Intensif. 98 (2015) 22–31.
[15] M.S.R. Abbott, et al., Liquid culture of microalgae in a photobioreactor (PBR) based on oscillatory baffled reactor (OBR) technology—a feasibility study, Chem. Eng. Sci. 138 (2015) 315–323.
[16] P. Lutze, et al., A systematic synthesis and design methodology to achieve process intensification in (bio) chemical processes, in: S. Pierucci, B.G. Ferraris (Eds.), 20th European Symposium on Computer Aided Process Engineering, 2010, pp. 241–246.
[17] P. Lutze, R. Gani, J.M. Woodley, Process intensification: a perspective on process synthesis, Chem. Eng. Process. 49 (6) (2010) 547–558.
[18] S.D. Barnicki, Separation System Synthesis: A Knowledge-Based Approach, The University of Texas, Austin, 1991.
[19] S. Lowenkron, Amines, aromatic, methylenedianiline, Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, Inc., 2000.
[20] S.D. Barnicki, J.R. Fair, Separation system synthesis: a knowledge-based approach. 1. Liquid mixture separations, Ind. Eng. Chem. Res. 29 (3) (1990) 421–432.
[21] S.D.F. Barnicki, R. James, Separation system synthesis: a knowledge-based approach.2. Gas/vapor mixtures, Ind. Eng. Chem. Res. 31 (7) (1992) 1679–1694.