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Reference:

Muñoz López Carlos André, Telen Dries, Nimmegeers Philippe, Cabianca Lorenzo, Logist Filip, Van Impe Jan.- A process simulator interface for multiobjective optimization of chemical processes
Computers and chemical engineering - ISSN 1873-4375 - 109(2018), p. 119-137
Full text (Publisher's DOI): <https://doi.org/10.1016/J.COMPCHEMENG.2017.09.014>

A process simulator interface for multiobjective optimization of chemical processes

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Abstract

The (bio)chemical process industry is under an increasing pressure due to smaller margins and increasing societal and legislative demands for a sustainable future. In this context model-based optimization contributes to the solution because it serves to improve the processes' performance. Furthermore, multiobjective optimization techniques provide the decision maker with a deeper insight in the tradeoffs when choosing an operating condition. However, an accurate process model is needed to apply these techniques efficiently. In this paper, a novel interface is developed between state-of-the-art gradient-based optimization techniques and the widely used process simulator Aspen Plus. Furthermore, specific challenges and solutions for overcoming the gap between process simulators and optimization tools are highlighted. The resulting interface allows gradient-based techniques to be exploited for optimization of complex industrial processes modeled in the advanced Aspen Plus environment. The interface ensures constraints satisfaction, and a higher computational performance than gradient free methods.

Keywords: Multiobjective optimization, Gradient-based optimization, Process optimization, Aspen Plus

1. Introduction

In light of the societal and legislative pressure on the process industry to increase its sustainability and to remain competitive in a more globalized world, model-based process optimization can play an important role both in process design and operation (Liu and Huang, 2012; Ren et al., 2016). When optimizing (bio)chemical

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6 processes, conflicting objectives are often present (Logist et al., 2009; Vallerio et al.,
7 2015). A common example is the search for higher profitability while improving the
8 safety of operation and reducing the energy consumption. However, the frequent
9 influence of *inconmeasurable* parameters makes their numerical weighting into a
10 single (economical) function practically infeasible. Therefore, a more informative
11 approach is to provide the decision maker with a thorough view on the set of pos-
12 sible optimal solutions, in such a way that the sensitivity of the solutions and/or
13 opportunity cost of the decision can be evaluated. Hence, the optimization method-
14 ology considered in this work is focused on dealing simultaneously with multiple and
15 conflicting objectives, generating as result a set of possible solutions which offer the
16 different tradeoffs between the objectives of interest.

17
18 Before model-based optimization can be performed, an accurate process model is
19 required. For some applications this entails developing and executing costly exper-
20 iments (Espie and Macchietto, 1989; Van Derlinden et al., 2010; Telen et al., 2014).
21 In many process engineering approaches however this can be obtained by means of a
22 process simulator. In this paper, Aspen Plus is considered as process simulator as it
23 is widely used for the design and operation of chemical processes. However, it does
24 not include advanced multiobjective optimization algorithms, which normally are
25 able to generate valuable tradeoff knowledge of the investigated process models and
26 can be expected to improve the process insight significantly. In the case of gradient-
27 based optimization algorithms though, actual knowledge on the model equations is
28 required, either the system of equations itself or sufficient information on the size,
29 structure and gradient of the system, hence limiting its implementation to cases
30 for which this information is available or can be formulated. This limitation mo-
31 tivates this work in which a connection between a widely used commercial process
32 simulator and state-of-the-art gradient-based optimization techniques is established.

33
34 The solution of a multiobjective optimization (MOO) problem can be performed by
35 a wide variety of algorithms. According to Ramzan and Witt (2006) the solution
36 approaches can be divided in two: *ideal multiobjective optimization* procedures and
37 *preference-based multiobjective optimization* procedures. This is equivalent to what

Logist et al. (2010) discuss when dividing the methods in vectorization and scalarization techniques. In both references the former case corresponds to methods that can directly tackle the MOO problem and produce at once a representation of the Pareto front. Information coming from the decision maker is then used to select one of the tradeoff solutions. Stochastic evolutionary algorithms, Genetic Algorithms (GA) and particle swarm optimization for multiple objectives are examples of these methods (Rangaiah and Bonilla-Petricolet, 2013). The latter case on the other hand corresponds to methods which reformulate the MOO into one or multiple parametric single objective problems to solve them individually.

Rangaiah and Bonilla-Petricolet (2013) subclassify the scalarization methods depending on two features: the introduction of the decision maker's preferences and the possibility to obtain one or multiple solutions. Classical scalarization methods which require *a priori* decision maker's information, produce only one non-dominated solution. If multiple solutions are desired, it is required to program a sequence of different problems with different values for the parameters. Some examples of the former category are the weighted methods (e.g., global criterion, weighted sum, weighted min-max, weighted product, exponential weighted), ϵ -constraint and the goal programming methods (Miettinen, 1999). In contrast, examples of the latter are Normal Boundary Intersection (NBI) (Das and Dennis, 1998) and Normalized Normal Constraint (NNC) (Messac et al., 2003) where the preference is articulated *a posteriori* or interactively (Logist et al., 2010; Vallerio et al., 2015).

In this contribution, some selected methods for the vectorization and scalarization approaches are applied. The aim is to compare their performance on the process simulator interface using a debutanizer column model as an illustrative case study, and to highlight the advantages of the proposed gradient-based approach using the scalarization methods. Some of these advantages are a better performance in terms of computational time and a higher accuracy to tackle constrained problems (Logist et al., 2013). In the last part the interface using scalarization methods is exploited for the optimization of two industrially relevant case studies, the butyl acetate production process and the methanol production via methane tri-reforming.

70

71 Enabling MOO in a process simulator is not straightforward. The most common
 72 approach found in literature employs *black box optimization* which does not require
 73 model information. This type of interfaces between the process simulator and the
 74 optimization algorithm are built to transfer model evaluation values (dependent
 75 variables) and the iterative values of the decision variables (independent variables).
 76 In this direction, Diwekar et al. (1992) proposed a Mixed Integer Nonlinear Pro-
 77 gramming (MINLP) synthesizer using Aspen Plus through a stochastic annealing
 78 algorithm. Tarafder et al. (2005) implement NSGA-II (Deb et al., 2002) to ap-
 79 ply MOO of a simulated industrial styrene monomer manufacturing process. Jang
 80 et al. (2005) developed a hybrid genetic algorithm that introduces a quadratic
 81 search in a region defined after some generations of the GA, and coupled it to As-
 82 pen Plus. Gutierrez and Briones (2009) use NSGA-II in the MOO of a rigorous
 83 model for Petlyuk sequences in Aspen Plus. Similarly Bravo et al. (2010) use GA
 84 in the design and optimization of a Extractive Dividing Wall Column. Eslick et al.
 85 (2011) present a framework for the MOO of processes using Aspen Plus models,
 86 Excel and modeFRONTIER, where the optimization algorithm is NSGA-II. Taras
 87 and Woinaroschy (2012) use NIMBUS algorithm (Miettinen, 1999) and a GA in an
 88 interactive MOO framework, interfacing SuperPro Designer and Matlab. Finally,
 89 Wang and Feng (2013) optimize the hydrogen production in a refinery modeled in
 90 Aspen Plus using NSGA-II.

91

92 In contrast, to exploit gradient-based optimization algorithms, either the set of
 93 model equations is made available or sufficient gradient information is provided di-
 94 rectly to the solver. Only few cases are found to be based on the availability of
 95 the model equations. Hakanen et al. (2006) developed an integrated multiobjective
 96 design tool for process design using BALAS which is a steady state simulation pack-
 97 age for chemical processes with emphasis on pulp and paper processes. Bortz et al.
 98 (2014) propose a scheme for MOO acquiring the required model information from
 99 the available source code of CHEMASIM which is an equation oriented steady-state
 100 flowsheet simulator developed by BASF SE. On the contrary, most of the flowsheet
 101 simulators do not make the system of model equations available. Therefore, differ-

ent approaches have been investigated to provide the gradient information to the Nonlinear Programming (NLP) solvers. Harsh et al. (1989) exploited the derivative information available from an optimization problem formulated in FLOWTRAN to interface it with a Mixed-Integer Nonlinear Programming (MINLP) algorithm and accomplish the retrofit of an ammonia process. Diaz and Bandoni (1996) proposed, using the same flowsheet simulator, to estimate numerically the gradient information by finite differences and using it in the MINLP formulation for the optimization of an ethylene plant. Based as well in numerical estimation of the gradient information, Navarro-Amoros et al. (2014) introduce a framework for integrating chemical process simulators, explicit equations and third party models with gradient based optimization.

A slightly different approach is the use of the *equation set object* (ESO). This approach relies on interfacing a set of information (e.g., gradient and variable information) which is defined according to CAPE-OPEN standards (Lang and Biegler, 2007). This interface allows access to the structure of the model (i.e., the number of variables and equations, and the sparsity pattern of the Jacobian), as well as to information on the involved variables (i.e., their names, current values, and lower and upper bounds) (Leineweber et al., 2003). Some examples are presented by Leineweber et al. (2003) at optimizing dynamic processes using MUSCOD-II and by Lang and Biegler (2007) whom developed the software tool DynoPC to optimize dynamic processes modeled in gPROPMS.

Alternatively to process simulators that support the CAPE-OPEN standard, other simulator packages have developed equivalent strategies to be interfaced with optimization algorithms. In Chen et al. (2009) an IPOPT based solver and CAPE-OPEN solvers were encapsulated and embedded into the *Aspen custom modeler* via the Aspen Open Solvers (AOS) interface using Dynamic Link Libraries (.dll files). This shows that the AOS interface supports similar operations to the ESO interface. However, in the case of the AOS interface, the model information is not handled out of the process simulator but the optimization algorithm is embedded into the simulation instead, reducing significantly the flexibility of the interface and

134 making it less accessible. Alternatively to the AOS approach, the Open Object
135 Model Framework (OOMF) included within the AspenTech software packages of-
136 fers programmatic access to the equation-oriented engine (Aspen, 2011). In this
137 contribution the OOMF is exploited to develop an interface with similar capabil-
138 ities to an CAPE-OPEN ESO interface for Aspen Plus. This interface allows the
139 connection of Aspen Plus to gradient-based MOO methods, such that Pareto op-
140 timal points can be computed more efficiently using gradient information from the
141 model that has been computed analytically by the Equation Oriented (EO) engine.
142 Furthermore, the specific challenges and solution approaches for the use of process
143 simulator models in optimization tools are highlighted. This contribution is ex-
144 pected to provide users with an increased insight in the process operation and allow
145 for a more informed decision.

146

147 The paper is structured as follows. Section 2 introduces the mathematical for-
148 mulation of MOO and describes the employed methods. In section 3, the strategy
149 and the developed interface are discussed, it covers aspects on the optimization tool
150 and the process simulator Aspen Plus. The description of the three considered case
151 studies is provided in section 4. The obtained numerical results are presented and
152 discussed in section 5. The conclusions are summarized in the final section of the
153 paper.

154 2. Multiobjective optimization

155 In this section the mathematical formulation of the considered MOO problems
156 is presented. Subsequently the employed MOO techniques are discussed.

157 2.1. Mathematical formulation

158 Multiobjective optimization (MOO) refers to the simultaneous optimization of
159 two or more objective functions which are typically conflicting. In practice this
160 means that by improving one of the objectives another is worsened. The formulation
161 of a MOO problem considered in this paper is given by:

$$\min_{\mathbf{u} \in R^{n_u}} [J_1(\mathbf{x}, \mathbf{u}), \dots, J_n(\mathbf{x}, \mathbf{u})] \quad (1a)$$

subject to:

$$\mathbf{0} \geq \mathbf{g}(\mathbf{x}, \mathbf{u}) \quad (1b)$$

$$\mathbf{b}_l < \mathbf{u} < \mathbf{b}_u \quad (1c)$$

$$\text{with: } \mathbf{y} = [\mathbf{u}^\top, \mathbf{x}^\top]^\top \quad (1d)$$

162 In this formulation $\mathbf{J} \in R^n$ is the set of objective functions defined by independent
 163 variables (controls) $\mathbf{u} \in R^{n_u}$ and dependent variables (states) $\mathbf{x} \in R^{n_x}$. The rela-
 164 tion between the two set of variables is given by a fully determined system of model
 165 equations $\mathbf{0} = \mathbf{f}(\mathbf{x}, \mathbf{u})$ with $\mathbf{f} \in R^{n_x}$. These are the flowsheet equations solved inde-
 166 pendently by the process simulator and they represent e.g., thermodynamics, mass
 167 and energy balances and reaction kinetics. The vector $\mathbf{y}$ is used in view of concise-
 168 ness to represent the set of variables with a total number of variables $n_y = n_x + n_u$.
 169 The vector $\mathbf{g}$ denotes the n_c equality and inequality constraints of the problem.
 170 Additionally, in this formulation the lower ($\mathbf{b}_l$) and upper bounds ($\mathbf{b}_u$) for the in-
 171 dependent variables are explicitly established as boundary constraints (Rangaiah
 172 and Bonilla-Petricolet, 2013).

173

174 The *feasible space* Ω of the optimization problem is defined as the set of vectors
 175 $\mathbf{y}$ which satisfy all the constraints and bounds set in Equations (1b), (1c) and (1d).
 176 The difference between *single objective optimization* (SOO) and *multiobjective opti-*
 177 *mization* (MOO), is that finding a unique vector $\mathbf{y}$ which optimizes simultaneously
 178 all conflicting objectives is not possible. Consequently for a MOO problem a set of
 179 vectors $\mathbf{y}^*$ is found as *Pareto-optimal*. A point $\mathbf{y}^* \in \Omega$, is Pareto optimal iff there
 180 does not exist another point, $\mathbf{y} \in \Omega$, such that $J_j(\mathbf{y}) \leq J_j(\mathbf{y}^*)$ for all $j \in 1, \dots, n$
 181 and $J_i(\mathbf{y}) < J_i(\mathbf{y}^*)$ for at least one objective function i (Vallerio et al., 2015).

182

183 The solution of a MOO problem and the construction of its Pareto front can be
 184 perform following two approaches (Logist et al., 2010): vectorization and scalariza-
 185 tion methods.

186 2.2. Scalarization methods

187 Scalarization methods transform the multiple objective optimization problem
 188 (MOOP) into a (series of) parametric single objective optimization problems. There-
 189 fore, they do not tackle directly the whole MOOP but they still can produce mul-
 190 tiple non-dominated results by solving the parametric single problems sequentially.
 191 Additionally, since these methods often exploit deterministic gradient-based opti-
 192 mization approaches they tend to be fast and are able to account efficiently for
 193 constraints both on decision variables as well as dependent variables (Logist et al.,
 194 2010, 2013).

195
 196 In this contribution two scalarization methods are implemented, the Normal Bound-
 197 ary intersection (NBI) and the Normalized Normal constraint (NNC). These methods
 198 are able to cope with the intrinsic drawbacks of the simpler *a priori* scalarization
 199 methods (e.g., weighted sum, and ε -constraint). They produce a uniform spread of
 200 points on the Pareto front, covering non-convex segments as well, and the solution
 201 is independent of the objectives' scale (Logist et al., 2010).

202
 203 These two methods are based on a geometric approach of the objective function
 204 space. The *anchor points* i.e., the individual minimization of each of the different
 205 objectives, are determined first, subsequently a convex combination is used to re-
 206 formulate the problem following two different approaches. NBI (Das and Dennis,
 207 1998) searches for the Pareto optimal points over (quasi-)normal lines to the convex
 208 combination plane, looking for the points in the feasible objective space that are
 209 closest to the *utopia point*, i.e., the point consisting of all the individual minima.
 210 Meanwhile NNC (Messac et al., 2003) looks for optimal solutions for one of the orig-
 211 inal objectives but in a reduced version of the feasible space. This is constrained
 212 by *normal hyperplanes* based on the remaining objective functions. The detailed
 213 formulation and description of the resulting optimization problems can be found
 214 in Logist et al. (2010).

215 2.3. Vectorization methods

216 Vectorization methods are typically based on stochastic search procedures by
 217 sequential evaluations of the objective functions. The main feature is the ability to

tackle directly the MOO problem and to produce multiple non-dominated results simultaneously. Additionally, they are considered as easy to implement, flexible to be coupled with process simulators and generally regarded as global optimization approaches (Logist et al., 2010). The higher capability of these methods to determine global optimal solutions is mainly based on random search with multiple sampling in the feasible space and it is improved if multiple non-dominated individuals are kept simultaneously so the chances are higher for finding a path that leads to a global solution. The model is treated as a black box and therefore model information is not required (Bortz et al., 2014). Specifically, the elitist Nondominant Sorting Genetic Algorithm (NSGA-II) (Deb et al., 2002) is frequently used for solving many chemical engineering applications. The NSGA-II method is chosen as the vectorization approach to solve MOO problems in this contribution.

NSGA-II is an improved version of the NSGA algorithm (Srinivas and Deb, 1994). It is an evolutionary algorithm (EA) based on a multiobjective genetic algorithm. It follows the Goldberg ranking method (Goldberg, 1989) in the fitness assignment and evaluation, which is based on the Pareto optimality or Pareto ordering. Furthermore, NSGA-II uses the *crowded distance* and the *crowded tournament selection* strategies to preserve the diversity among solutions in the Pareto front while it preserves non-dominated individuals found at intermediate generations (Nakayama et al., 2009).

3. The interface between a process simulator and an optimization tool

In this section the developed interfaces linking the process simulator to the optimization tool are discussed. The first interface is for the black box optimization approach while the second one is aimed at gradient-based optimization by accessing the so-called *equation set object*. Detailed information is presented on how the complete simulation-optimization scheme is implemented. First, the description of the employed software tools is presented. Subsequently, the requirements of the interface and the proposed solution are discussed.

247 3.1. Software tools

248 Matlab R2014b is used as optimization platform. It allows to implement a
 249 wide variety of optimization algorithms, using embedded functions, as part of the
 250 optimization toolbox, or scripted by the user. This contribution aims to com-
 251 pare the vectorization and scalarization approaches, and Matlab offers the required
 252 flexibility to implement multiple optimization algorithms. On the one hand, the
 253 NSGA-II method is employed via Matlab's function *gamultiobj*. This is a variant
 254 of NSGA-II created to run on Matlab's environment (Bau et al., 2015). On the
 255 other hand, algorithms for NBI and NNC are scripted in the CasADi environment.
 256 CasADi is a symbolic framework for automatic differentiation and numerical op-
 257 timization (Andersson et al., 2012), which additionally provides an interior point
 258 method (IPOPT (Wächter and Biegler, 2006)) to solve the resulting NLP problems.
 259 Finally, Aspen Plus is used as process simulator, it offers EO mode (Apen, 2005),
 260 which guarantees handling gradient information of the model equations.

261
 262 IPOPT is exploited along this work to solve the NLPs resulting from the appli-
 263 cation of the NBI and NNC methods to the MOOPs. This method is based on the
 264 application of the interior point method or *barrier method* to solve inequality con-
 265 straints. Line search methods are applied for the solution of the IPOPT problem,
 266 therefore gradient information is needed. In this work a low rank update based on
 267 the BFGS scheme is used (Nocedal and Stephen, 1999), because the exact Hessian
 268 is not available.

269 3.2. Interface description

270 Three different approaches are identified for interfacing process simulators and
 271 optimization algorithms, i.e., *black box optimization*, *access to the equation set ob-*
 272 *ject* and *access to the set of model equations*. The main difference between the three
 273 approaches is what information is transferred to the external optimization tool.

274
 275 **Black box optimization:** This is a well-known and often exploited approach
 276 for interfacing a process simulator and complex stochastic optimization algorithms
 277 (e.g., Aspen Plus and NSGA-II being executed on Matlab or Visual basic). This
 278 approach is based on exploiting the information contained in successive objective

function evaluations since the model remains unknown. There exist several references based on this approach. For example, Gerali and Romagnoli (2015) present an optimization framework using a multiobjective stochastic optimization approach to incorporate tradeoffs between cost and financial risk for the design of integrated biorefineries. However, there are limitations in applying this approach. For example in the case of using NSGA-II, it has been reported that the performance decreases if other constraints than simple bounds for the decision variables are included (Logist et al., 2013). In this work black box optimization will be implemented for comparison.

Access to equation set object (ESO): This approach refers to implementing the ESO interface defined according to CAPE-OPEN standards. This is transferring a set of information derived from the model but not the model equations. The set of information is defined as the minimum required to execute gradient-based optimization algorithms. Different from the identified references following this approach Leineweber et al. (2003), Schopfer et al. (2005), Lang and Biegler (2005), Lang and Biegler (2007), which all used *gProms*, Aspen Plus does not support this standard. Therefore the approach presented in this contribution exploits OMF to get programmatic access to the equation oriented engine and querying the same minimal information provided by an ESO interface. Taking advantage of this feature, an ESO equivalent interface is constructed to link Aspen Plus and Matlab. This interface has the capability of efficiently exploiting gradient-based optimization algorithms.

Access to the set of model equations: This approach is the ideal approach from an optimization point of view. It could require a single interaction between process simulator and optimizer, i.e., the transfer of the set of model equations. Therefore, this approach can result in a high performance. Unfortunately it is limited by the typically constrained access to model equations in process simulators. Only few cases exist in the literature following this approach. In Sadrieh and Bahri (2011) an implementation is presented using models from Aspen Plus via Aspen Custom Modeller (ACM). However, this is a highly complex procedure that re-

311 quires additional program utilities to interpret the process model and to integrate
 312 the complete implementation into ACM. Therefore, limiting the applicability and
 313 iteration with the optimization solver. Consequently this approach has not been
 314 followed in this work.

315 *3.3. Interface architecture*

316 The conceptual architecture for the developed interface of this contribution is
 317 the result of four components, i.e., the simulation software, the middleware, the
 318 wrapper protocol and the optimization platform. Figure 1 represents this struc-
 319 ture graphically, where the interface is strictly formed by the middleware and the
 320 wrapper protocol (dashed line). On the one hand the middleware protocol is imple-
 321 mented to allow partial automation of the process simulator and to transfer in both
 322 directions the required information. Some middleware protocols are ActiveX(COM)
 323 and CORBA. On the other hand the employed wrapper protocol serves to interpret
 324 the information transferred by the middleware and transform it on useful informa-
 325 tion that can be exploited either by the optimization algorithm or simulator.

326
 327 The type of optimization to be performed, i.e., either black box or accessing the
 328 ESO, determines what type of information needs to be transferred and which in-
 329 teractions have to be enabled between the process simulator and the optimization
 330 platform. In case of black box optimization, it consists of only the values of the
 331 dependent and independent variables for which read and writing actions should be
 332 allowed. In contrast when gradient-based optimization is aimed at, more complex
 333 information structures and actions have to be considered. The ESO CAPE-OPEN
 334 standard is used as reference to define what should be considered on the interface
 335 (CO-LaN, 2003):

- 336 • Obtain the current values of a specified subset of the variables (controls and
 337 states).
- 338 • Alter the values of any specified subset of the independent variables (controls).
- 339 • Get the structure of the sparse matrix representing the partial derivatives of
 340 a specified subset of the equations with respect to a specified subset of the
 341 variables.

- 342 • Compute the residuals of any specified subset of the equations at the current
 343 variable values.
- 344 • Get a sparse matrix containing the values of the partial derivatives of a spec-
 345 ified subset of the equations with respect to a specified subset of the variables
 346 (at the object's current variable values).

347 The implementation of the two selected approaches, black box optimization and
 348 optimization accessing the ESO, can be graphically represented by Figures 2 and
 349 3 respectively. The interface constructed in both cases (middleware and wrapping
 350 protocol) can be described as the result of two sub-interfaces: (i) a control interface
 351 (dash line), and (ii) an information interface (dotted line). A more detailed discus-
 352 sion on some specific aspects that were considered to establish these interfaces are
 353 split in the following four parts: (i) simulation, (ii) control interface, (iii) informa-
 354 tion interface, and (iv) optimization.

355
 356 **Simulation:** Here the appropriate strategy of solution should be established, i.e.,
 357 *sequential modular* or *equation oriented*. While for black box optimization it is pos-
 358 sible to run the simulation in any mode, for the optimization accessing the ESO it
 359 is restricted to *equation oriented*.

360 **Control interface:** As a common feature for both approaches the *ActiveX* frame-
 361 work is used to construct the control interface, it enables communication within
 362 applications running on Windows.

363 **Information interface:** This is intended to transfer the required data. Therefore,
 364 it follows different schemes for the two distinct optimization approaches, due to
 365 the nature of the information to be transferred. The information interface for the
 366 black box optimization approach uses additional features of the *ActiveX* interface.
 367 Numerical values of a given set of variables (dependent and independent variables)
 368 are transferred. As explained before, since Aspen Plus does not supports the ESO
 369 CAPE-OPEN standard, an alternative approach is followed exploiting the Open
 370 Object Model Framework (OOMF). A detailed description of the script language
 371 used by the OOMF kernel is given in Aspen (2011). The middleware in this case
 372 is defined as a set of ASCII and text files that contain the required data. These
 373 are sucesively accessed to take the information either by Aspen Plus or Matlab, in

each direction. The structure given to the middleware consist of three main files. The first one contains variables information, i.e., variable name, values, scale factor, specification, and units. The second file, corresponds to the equations' information including the residual values. Finally, the last file is created to report the Jacobian. Hence all this information is generated every time the simulation converges and serves to provide the optimization routine in Matlab with the required elements at each NLP solver iteration.

Due to its dependence on creating ASCII and text files, the middleware is considered as a bottleneck for the computational performance of the proposed approach. However, it is at the authors' current best knowledge the only way provided by the OOMF to retrieve the gradient information available in the equation oriented engine of Aspen Plus. Later, the case studies show that the possible restriction imposed by this feature is compensated by the higher performance and accuracy obtained since analytically derived gradient information is being retrieved. This overcomes the main limitation of previous gradient-based approaches which depend on the numerical estimation of the gradient information through finite differences (Diaz and Bandoni, 1996; Navarro-Amoros et al., 2014). Nosedal and Stephen (1999) report that the finite differences approximation requires n (*forward-difference*) or $2n$ (*central-difference*) more evaluations of the objective/constraint functions than the analytic differentiation, to evaluate the Jacobian. With n being the number independent variables.

In Matlab, the wrapper function interprets the information collected from the files according to Equation 2. The assumption $\mathbf{R} \approx \mathbf{0}$ is taken based on the fact that the EO engine in Aspen Plus internally solves the system of model equations by finding the values of the dependent variables $\mathbf{x}$ that minimize the residual (Apen, 2005). For this the EO engine utilizes analytical first order derivatives of the model equations and a numerical perturbation method in cases the analytical differentiation is not possible. Therefore, this guarantees the availability of the required gradient information while the residual values ($\mathbf{R}$) correspond to the error after convergence of the system of equations. These can later be used to evaluate the validity of

the results reported by the simulation. However, it should be considered that the assumption $\mathbf{R} \approx \mathbf{0}$ introduces "noise" to the NLP solver because the states and therefore the Jacobian values are not exact.

$$\begin{bmatrix} f_1(\mathbf{x}, \mathbf{u}) \\ f_2(\mathbf{x}, \mathbf{u}) \\ \vdots \end{bmatrix} = \begin{bmatrix} R_1 \\ R_2 \\ \vdots \end{bmatrix} \approx \mathbf{0} \quad (2)$$

$$\text{Jacobian} = \frac{\partial \mathbf{f}}{\partial \mathbf{y}} = \begin{bmatrix} \frac{\partial f_1}{\partial y_1} & \dots & \frac{\partial f_1}{\partial y_{n_y}} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_{n_e}}{\partial y_1} & \dots & \frac{\partial f_{n_e}}{\partial y_{n_y}} \end{bmatrix}$$

Optimization: The routine for the black box optimization approach is based on NSGA-II. The MOO approach accessing the ESO is performed based on the NBI and NNC scalarization methods. For these methods the NLP solver has to be provided with the corresponding gradient information of the model at each iteration. Therefore a *Callback* structure for functions is implemented. This is a method in IPOPT for defining routines that should be executed at each iteration. Internally the *Callback* function is formulated to communicate the values of the controls, generated at each iteration of the NLP solver to the Aspen simulation via the information interface. Then the Aspen simulation runs to generate new results, which are gathered back to the *Callback* function in Matlab via the second part of the information interface. At this point the collected information is transformed into elements that can be handled by the IPOPT method. As a gradient-based NLP solver, IPOPT depends on the evaluation of the gradient of the objective and constraint functions with respect to the controls. Since the gradient information received from the information interface is the Jacobian in the form given by Equation (2), it is split into two matrices, one containing the partial derivatives with respect to the controls while the other contains the partial derivatives with respect to the states. Afterwards, the sensitivity matrix (Ascher and Petzold, 1998) (i.e., the inverse of the partial derivatives with respect to states) is operated according to Equation 3 to get the partial derivatives of the states with respect to the control variables, which in turn are required by IPOPT to fully establish the gradient of the objective and constraint functions according to Equation 4.

$$\frac{\partial \mathbf{x}}{\partial \mathbf{u}} = \begin{bmatrix} \frac{\partial x_1}{\partial u_1} & \dots & \frac{\partial x_1}{\partial u_{n_u}} \\ \vdots & \ddots & \vdots \\ \frac{\partial x_{n_y-n_u}}{\partial u_1} & \dots & \frac{\partial x_{n_y-n_u}}{\partial u_{n_u}} \end{bmatrix} \quad (3)$$

$$\frac{\partial \mathbf{x}}{\partial \mathbf{u}} = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \dots & \frac{\partial f_1}{\partial x_{n_y-n_u}} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_e}{\partial x_1} & \dots & \frac{\partial f_e}{\partial x_{n_y-n_u}} \end{bmatrix}^{-1} \begin{bmatrix} \frac{\partial f_1}{\partial u_1} & \dots & \frac{\partial f_1}{\partial u_{n_u}} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_e}{\partial u_1} & \dots & \frac{\partial f_e}{\partial u_{n_u}} \end{bmatrix}$$

$$\nabla_u \begin{bmatrix} \mathbf{J}(\mathbf{y}) \\ \mathbf{g}(\mathbf{y}) \end{bmatrix} = \begin{bmatrix} \nabla_u \mathbf{J}(\mathbf{u}, \mathbf{x}) \\ \nabla_u \mathbf{g}(\mathbf{u}, \mathbf{x}) \end{bmatrix} = \begin{bmatrix} \mathbf{p}(\frac{\partial \mathbf{J}}{\partial \mathbf{u}}, \frac{\partial \mathbf{J}}{\partial \mathbf{x}} \frac{\partial \mathbf{x}}{\partial \mathbf{u}}) \\ \mathbf{q}(\frac{\partial \mathbf{g}}{\partial \mathbf{u}}, \frac{\partial \mathbf{g}}{\partial \mathbf{x}} \frac{\partial \mathbf{x}}{\partial \mathbf{u}}) \end{bmatrix} \quad (4)$$

In order to make the gradient information available to IPOPT, two different approaches have been implemented:

Linearization of the states:. Linear functions were formulated in the form $\mathbf{x} \approx \frac{\partial \mathbf{x}}{\partial \mathbf{u}} \mathbf{u} + \mathbf{C}$ to represent the system of flowsheet equations in the process simulator. These are valid only locally and therefore are updated at each iteration of the IPOPT solver with the values for $\frac{\partial \mathbf{x}}{\partial \mathbf{u}}$ and $\mathbf{C}$. This is a dummy formulation that serves only to transfer the gradient information to the IPOPT routine.

Embedding a function and its Jacobian:. Alternatively a more complex programming structure involves developing functions for embedding the states as callback functions with a known Jacobian matrix ($\frac{\partial \mathbf{x}}{\partial \mathbf{u}}$) in CasADi. This approach offers the same numerical outcome as the previous one, but the differentiation of the states in Matlab is not needed during the optimization. As part of the first case study these two approaches will be compared.

The developed Interface for gradient-based MOO of processes simulated in Aspen Plus is referred as INPROP (INterface for PRocess OPTimization). The Matlab scripts that constitute this software tool are made freely available for academic purposes on the website <https://cit.kuleuven.be/biotec/software/inprop-1>. Complete details on the described interface can be found in these scripts. Additionally, the files corresponding to the three implemented case studies are available as well in

452 this website as supplementary files.

453 4. Case studies

454 In the first subsection the debutanizer column case study is presented. It is
455 used as an illustrative case to evaluate and compare the performance and limita-
456 tions of the methods implemented in the optimization interface, i.e., scalarization
457 and vectorization methods. The butyl acetate and the methanol production pro-
458 cesses are introduced as more complex case studies to exploit the developed op-
459 timization interface with the gradient-based scalarization approach in industrially
460 relevant flowsheets.

461 4.1. Debutanizer

462 The debutanizer column is a common distillation unit in refineries, it is
463 used as part of different processes to fractionate light products. For instance on a
464 delayed coking unit the debutanizer column is part of the vapor recovery section
465 where an improved separation between the gas and naphtha coming from the de-
466 layed coking unit is achieved. The implemented Aspen simulation for this process
467 is made available as the Supplementary file A. In Figure 4 the simulated column
468 with the independent and dependent variables is presented. The composition of the
469 feed stream is presented in Table 1. Some approximations used in the simulation
470 for this composition are the following: (i) the butenes are approximated by pure 1-
471 butene, (ii) fractions defined by range of boiling points are approximated by a single
472 compound (hydrocarbon) with a boiling point in the middle of the range. For the
473 C_5 - 453.15 K fraction, n-heptane is being used, this alkane boils at 373.15 K. For
474 the 453.15 K - 623.15 K fraction 1-pentadecane is used, as this alkane has a boiling
475 point at 544.15 K.

476
477 Two commonly used equations of state for this kind of systems are: (i) Peng-
478 Robinson (PR) and (ii) Soave-Redlich-Kwong (SRK). In Ahmadi et al. (2015) the
479 accuracy of a set of property methods for a debutanizer column regarding actual
480 real measurements is investigated finding that PR is the most accurate method
481 for this system. For the simulations the *Radfrac* method in Aspen Plus is chosen

in combination with the ideal equilibrium model. The latter differs from the rate based model as it does not take into account limitations due to heat-mass transfer and liquid-vapor diffusion. Additionally, the efficiencies for all trays are set equal to one. Other specifications needed for the simulations are introduced in Table 2. For this case study the *reflux ratio* (RR) and the *distillate rate* are to be used as the independent variables or controls in the optimization. The remaining states and an overview of the control variables are given in Table 3.

4.2. Butyl acetate production

A commercially viable chemical route to produce butyl acetate is based on the transesterification of methyl acetate (MeAc) using butanol (BuOH) (Tang et al., 2005). This category of reactions corresponds to an ester reacting with an alcohol in the presence of a catalyst. From this reaction a new couple ester-alcohol is produced due to the exchange of the organic groups present in the feed. In this case study the products are butyl acetate (BuAc) and methanol (MeOH) (Luyben et al., 2004). The exact chemical reaction is presented in Equation (5). This process has been proven to be economically feasible, because the MeAc, which is a low value side product from the production of poly-(vinyl)-alcohol (PVA), is converted into MeOH and high purity BuAc. The former product is recycled as feedstock for the PVA production (Steinigeweg and Gmehling, 2004) while the BuAc can be used in many applications and has a higher added value.

The complete production process requires multiple separation stages to achieve high purity outlet streams and recover most of the reactants. The main difficulty in this separation is the presence of two binary azeotropes in the mixture: (i) methyl acetate and methanol and (ii) butyl acetate and butanol (Luyben, 2011). Therefore multiple production approaches have been proposed. The traditional approach consist of a *Continuous Stirred Tank Reactor* (CSTR) followed by a set of separation columns, for which two techniques are commonly used: i.e., pressure swing distillation and the use of an entrainer (Jimenez et al., 2002). Several alternatives

to the traditional process have been investigated. Gangadwala and Kienle (2007) evaluates an option based on a reactive distillation column and side reactor coupled with non-reactive distillation columns. However, this case study is based on the traditional scheme using the pressure swing technique for the separation stage.

In Figure 5 the simulation flowsheet of the butyl acetate production process is presented. This corresponds to the simulation developed by Verheyden (2014) which in turn is based on the flow diagram and operation conditions for the process presented by Luyben et al. (2004). These operational conditions are used in this work as a benchmark to check the achieved improvements via process optimization. In the process the input streams consisting of MeAc and BuOH are brought into a CSTR at the given conditions. Inside the reactor the transesterification reaction takes place, as a reversible reaction, catalyzed by a strong acid (Wang et al., 2008). The reaction kinetics are given according to Equation 6. Some thermodynamic properties of this reaction are: (i) the equilibrium constant is close to the unit, therefore the dependence on the temperature is weak and (ii) the enthalpy of the reaction is low (Luyben et al., 2004). The outlet stream from the reactor, containing the four involved chemical substances is then sent to the first distillation column. From this the top product is rich in MeAc and MeOH while the bottom product is a mixture of mainly BuAc and BuOH. For the light product a second separation step is applied, in this case the top product is a mixture at almost the azeotropic MeAc-MeOH composition. This stream is recycled to the reactor. The bottom product of the second distillation column is almost pure methanol. Meanwhile the heavy product from the first distillation column is also subsequently separated, in this case into high purity BuAc as bottom product and a stream concentrated on BuOH, which is recycled to the reactor (Luyben et al., 2004).

$$\begin{aligned} r &= k_F C_{MeAc} C_{BuOH} - k_R C_{BuAc} C_{MeOH} \\ K_F &= 7 \cdot 10^6 e^{-71960/RT} \\ K_R &= 9.467 \cdot 10^6 \exp^{-72670/RT} \end{aligned} \quad (6)$$

Due to the complexity of the mixtures, for which two binary azeotropes occur, an activity model is required to describe the vapor-liquid equilibrium present in the

system. For this (Verheyden, 2014) uses NRTL in the simulation. Table 4 contains a summary of the fixed process conditions and parameters to model the butyl acetate production process, the detailed information can be found in the Supplementary file B. Table 5 presents the complete list of variables and states used to formulate the MOO problem.

4.3. Methanol production via methane tri-reforming

Traditionally one of the more common commercial routes to produce methanol is the catalytic conversion of syngas (gas mixture of carbon monoxide CO and hydrogen H_2). There exist many carbon sources that can be used as feedstock to obtain syngas. An increasing attention goes to production routes exploiting the valorization of side streams, renewable materials and waste, since value is added to these material streams with an environmentally positive impact. Recently particular attention has been focused to the methane tri-reforming, as an alternative approach for the conversion of CO_2 in the flue stack gas without the CO_2 pre-separation (Song and Pan, 2004). Thus producing methanol from methane and flue gas involves two reaction stages. First the tri-reforming, which is a complex thermo-chemical conversion involving several reactions to convert CH_4 , CO_2 , O_2 and H_2O into syngas. Zhang et al. (2013) present the set of 9 reactions normally related to this conversion. Secondly, for the methanol production, the syngas in a proportion H_2/CO around 2 is brought to reaction conditions to produce a mixture of MeOH and water. In Equation (7) the methanol production reactions are presented. The third reaction corresponds to the reversible water gas shift reaction (Navarro-Amoros et al., 2014).

Figure 6 corresponds to the flowsheet modeled in Aspen Plus for this case study. This is the production scheme proposed and studied by Zhang et al. (2013). In the process, the two gas streams (flue gas and methane) are put together and preheated

564 to the reaction temperature before entering into the reactor. The tri-reforming is
565 modeled in a Gibbs reactor which computes the composition at the outlet as the
566 equilibrium composition, that minimizes the total Gibbs free energy over all the
567 species, at the reactor conditions. The reactor output is then cooled down and
568 compressed. After achieving the desired reaction pressure for the methanol produc-
569 tion, the temperature is adjusted, cooling or heating is required depending on the
570 desired reaction temperature. As suggested by Zhang et al. (2013) the methanol
571 reactor is modeled as an equilibrium reactor considering only reactions (7a) and
572 (7b), since in these conditions the the water gas shift reaction is linearly depen-
573 dent and its conversion is negligible. As part of preliminary studies the CO and
574 CO_2 conversion of the modeled methanol reactor were validated with respect to the
575 values reported by Navarro-Amoros et al. (2014). This validation showed adequate
576 results in the range between 5 to 30 MPa and from 480 to 570 K. After reaction, the
577 gaseous product is expanded and cooled down to separate most of the methanol and
578 water from non-condensable gases. The gas separated in the flash drum contains
579 high levels of unreacted syngas due to the low conversion in the methanol reactor.
580 Therefore this stream is recirculated to the reactor. A purge is taken from the
581 recycle stream to avoid accumulation of inert gases (mainly N_2) in the loop. The
582 recycle stream has to be compressed to enter the reactor again. The liquid product
583 from the flash separation is then expanded again to reduce even further the amount
584 of non-condensable gases and then the remaining liquid is distilled to adjust the
585 quality of the methanol product to be $\geq 99,5\%$.

586

587 As suggested by Zhang et al. (2013), Peng Robinson equation of state was the
588 thermodynamic model implemented for this flowsheet simulation. The optimal
589 conditions reported by Zhang et al. (2013) were reproduced to serve as reference
590 and to evaluate the advantages of the results obtained via MOO of the process.
591 Following the same approach presented by Navarro-Amoros et al. (2014) the kinet-
592 ics of the methanol reactions were considered only to determine the reactor volume
593 required to achieve the equilibrium concentrations predicted in Aspen Plus. The
594 reader can find the kinetic models and parameters in Navarro-Amoros et al. (2014).
595 Table 6 contains a summary of fixed process conditions and parameters to model

the methanol production process, the detailed information can be found in the Supplementary file C. The independent variables were selected based on what previous studies have evaluated about this process (Zhang et al. (2013); Navarro-Amoros et al. (2014); Luyben (2010)), and what are considered to be the most important operational parameters for this process. Table 7 presents the complete list of independent variables and states involved in the formulation of the MOO problem.

5. Simulation results

Section 5.1 discusses the results for the debutanizer while the results for the butyl acetate and methanol production processes are presented in sections 5.2 and 5.3 respectively.

5.1. Debutanizer

As this case study serves to illustrate and compare the results obtained by applying the two possible MOO approaches, two different MOO optimization formulations are evaluated. The first problem is based on objective J_1 , which has no physical interpretation but was chosen to highlight the advantages and main issues of each approach. This function was formulated to exhibit two optimal solutions in the feasible space, and it is given according to:

$$J_1 = -\left(p_1 u_2 \frac{1}{p_2 x_3^2} + p_3 x_4 - p_4 x_1^2 - p_5 x_2 - p_6 x_3 - e^{p_3 u_1 u_2}\right)$$

$$\begin{aligned} p_1 &= 2.266 \cdot 10^{-3} & p_2 &= 185.185 \\ p_3 &= 7.854 \cdot 10^{-4} & p_4 &= 1.712 \cdot 10^{-5} \\ p_5 &= -1.626 \cdot 10^{-5} & p_6 &= 555.555 \end{aligned} \quad (8)$$

In contrast the second MOO problem is based on a realistic profit function for the debutanizer column (J_2). This is based on the formulation and the values presented by White (2012). This function considers the income as result of the price for both products which are affected by the quality. Different from the case evaluated in the reference, in this case a step increase in the price for the top product is applied through a logistic function, while a linear increase on the price is formulated for the bottom product. The costs correspond to the energy consumption and the raw material. The total is expressed in relative terms, based on the mass inlet flow.

621 This function is formulated in Equation 9. The logistic function that determines
 622 the price for the distillate product is defined to establish two conditions, a low
 623 quality product ($> 4\% C_5$) and a high quality product ($< 4\% C_5$).

$$\begin{aligned}
 J_2 &= -(\text{income} - \text{costs})/x_8 \quad [\$/\text{kg}] \\
 \text{income} &= u_2 \left(\frac{a_1}{1 + e^{(-a_2(x_3 - a_3))}} + a_4 \right) + x_4(a_5(x_5 + x_6 + x_7 - a_6) + a_7) \\
 \text{costs} &= a_8 x_7 + a_9(x_1 + a_{10}x_2)
 \end{aligned} \tag{9}$$

$$\begin{aligned}
 a_1 &= 0.240 & a_4 &= 0.480 & a_7 &= 0.740 & a_{10} &= 0.500 \\
 a_2 &= -500 & a_5 &= 8.0 & a_8 &= 0.740 \\
 a_3 &= 0.040 & a_6 &= 0.017 & a_9 &= 0.0140
 \end{aligned}$$

624 Two additional objective functions are specified to complete the two MOO formula-
 625 tions. The aim is to investigate conflicting objectives that are normally considered
 626 as accounted by the profit function. Constructing the Pareto front for this problem
 627 allows a sensitivity analysis on the tradeoffs between the different objectives to en-
 628 hance process understanding and to made a more thorough decision on the chosen
 629 optimal operational conditions. These functions are the total energy consumption
 630 J_3 and the quality of the distillate product J_4 . The former is defined as the sum
 631 of the condenser and reboiler duties, while the quality of the distillate product is
 632 established by the content of n-Pentane (nC_5) in the stream. Equation 10 denotes
 633 objective functions J_3 and J_4 . The constraints for this problem are the minimum
 634 quality for the bottom product and the controls boundaries, given in Equation 11.

$$\begin{aligned}
 J_3 &= \sum_{i=1}^2 |x_i| \quad [MW] \\
 J_4 &= x_3 \quad [wt.frac.]
 \end{aligned} \tag{10}$$

635

$$\begin{aligned}
 g(x) : x_5 - 0.01 &\leq 0 \\
 5 < u_1 &< 25 \\
 9000 < u_2 &< 25000
 \end{aligned} \tag{11}$$

5.1.1. Single objective optimization

Here only the illustrative objective function is considered in order to evaluate and compare performance aspects of the methods applied. In Figures 7 and 8 the obtained results are presented. These denote contour graphs where the axes correspond to the control variables, distillate rate (u_2) against reflux ratio (u_1), and the colored contour lines correspond to different value levels for the objective function. On these graphs the black dashed line represents the quality constraint ($g(\mathbf{x})$) when it is exactly equal to zero, which along with the contour lines were drawn from a sensitivity analysis. In the figures the red points correspond to the results at each iteration of the NLP solver while the blue marks are the (local) optimal points in each case. Two cases are presented for each approach. In the case of the optimization accessing the ESO (Figures 7a and 7b), the difference is the convergence to two distinct optimum solutions. Since the direction of convergence is determined by the initial guesses for the controls, the effect of two different initial values can be seen in the figures. For the case in Figure 7a the best known minimum is found with the initial guess $\mathbf{u}_0$ as $[20, 11000]$ while for Figure 7b the local minimum is obtained for $\mathbf{u}_0$ is $[20, 11500]$. This shows the need for applying globalization procedures like the multiple starting point search when using gradient based methods.

The black box optimization results for different parameter values of the *gamultiobj* function, are presented in Figures 8a and 8b. The former corresponds to the case when the problem is solved with the default values, the problem does not converge to a solution and remains iterating in the neighborhood of the optimal solution. Figure 8a is the result if the iteration is forced to stop. In addition to the no convergence problem, a limited accuracy for satisfying the imposed constraint is observed. As can be seen in Figure 8 most of the results are in the neighborhood of the constraint line however only a few of them are exactly on the line or above it which are the conditions for fulfilling the constraint $g(x) \leq 0$. This means that at least under the default parameters, the genetic algorithm has limitations for convergence and satisfaction of the inequality constraint. In order to overcome these limitations the effect of modifying some parameters has been investigated. Population size, function tolerance and maximum stall generations have been adapted. In general

the successful strategy has been to reduce population size, imposing milder stopping criteria and offering lower tolerance to validate constraint satisfaction. One of the closest solutions obtained from this evaluation is presented in Figure 8b. The chosen parameters to produce this solution are: population size = 10, function tolerance = $1 \cdot 10^{-4}$, maximum stall generations = 30 and constraint tolerance = $5 \cdot 10^{-4}$. A clear improvement is observed regarding the constraint satisfaction, however the result obtained is far from the optimal solution.

In Table 9 the numerical results are presented. Only the results for the cases where the best known optimum is obtained are reported. In the case of black box optimization the reported values corresponds to the solution presented in Figure 8b. Regarding the optimization accessing the ESO two sets of results are presented. These correspond to using the two methods implemented for transferring the gradient information to IPOPT. As it can be seen the difference on the results is not significant, being lower than 0.1% for the objective function. In terms of computational time, as expected the time required by the gradient-based approach is lower than the black box optimization, this should correspond with fewer evaluations required of the objective function and therefore lower time spent on the solution of the flowsheet simulation.

5.1.2. Multiobjective optimization

First, the bi-objective problem, using the illustrative function and the total energy demand (J_1 and J_3), is solved. The results for the optimization accessing the ESO, and the black box optimization are depicted in Figure 9. In both cases the optimization problem was solved defining a feasible space that guarantees the presence of the two known optimal solutions on the illustrative function. For the convergence of the black box optimization the quality constraint was imposed as design specification in the simulation. This guarantees fulfilling the constraint condition while simplifies the optimization problem so the NSGA-II method has to solve a constraint-free problem. Thus the limitation of the genetic algorithm to cope with constraints is surpassed, however this impose an extra limitation because the design specifications in Aspen Plus can be only equality conditions. In Aspen Plus a design specification is an additional equation that has to be solve in the

700 system. Additionally, some parameters of the *gamultiobj* function are adjusted dif-
 701 ferent from the default values. This is the function tolerance = $1 \cdot 10^{-2}$, maximum
 702 stall generations = 10, and Pareto fraction = 0.3. The last parameter is used to
 703 control the elitism of the genetic algorithm and in this case is adjusted to generate
 704 a Pareto front with the same number of points produced by the ESO approach, so
 705 the results are comparable.

706

707 In Figure 9 the results from both methods for the Pareto front are plotted together
 708 with the curve that describes the border of the feasible space for the problem. This
 709 is obtained via sensitivity analysis and contains exact solutions. From these results
 710 some aspects are highlighted. First, a high accuracy is observed on the results from
 711 both optimization methods, but with limited reproducibility of the Pareto front. In
 712 the case of the ESO approach non-optimal Pareto solutions are present, while for
 713 the black box optimization the optimal points do not represent a uniform spread
 714 over the Pareto front. The non-optimal Pareto solutions are solutions at the border
 715 of the feasible region, that are dominated by other point in the Pareto front. When
 716 this is verified, it can be observed that only the Pareto front obtained via black box
 717 optimization meets the condition for all its points. The Pareto front obtained from
 718 the ESO approach contains a sub-set of 4 solutions which are non-optimal Pareto
 719 points, because there are other solutions that for the same values of J_1 require lower
 720 energy J_3 . Therefore, the solution for this bi-objective problem is a discontinuous
 721 Pareto front due to the presence of two minimum points for one of the objective
 722 functions. Regarding the computational cost, Table 10 presents the time required
 723 for convergence in each case. The fastest performance is obtained again for the
 724 gradient-based approach.

725

726 Finally the MOO with three objectives is formulated, i.e., illustrative function J_1 ,
 727 total energy demanded J_3 and distillate quality J_4 are considered. In this case the
 728 feasible space is defined to be only in the region of the best known minimum for the
 729 illustrative function which is the desired result. In Figure 10 the solutions generated
 730 by black box optimization and accessing the ESO are depicted. The black box opti-
 731 mization approach produces a solution that is restricted to a line, this is presented

732 in the Figure with small circles(o). It is interesting to see how this solution links
733 the three anchor points, however it is only a subset of the Pareto points generated
734 by the ESO approach.

735

736 To efficiently solve MOO problems via ESO approach some adjustment on the
737 options for the IPOPT solver can be applied. This to guarantee convergence of the
738 solver and increase computational performance using milder termination conditions.
739 In Table 12, the used solver parameters are reported for the three case studies. Fi-
740 nally, the performance of the two optimization approaches is illustrated in Table
741 10. These correspond to the solutions depicted in Figure 10. The high efficiency
742 of the black box optimization should be noted. However, it should be considered
743 that in this case the result is limited to just one part of the Pareto front generated
744 via the ESO approach. Therefore it offers a very limited amount of information. A
745 similar behavior has been discussed by Logist et al. (2013). Note that in general
746 for all results the performance of the gradient-based approach performs worse with
747 the embedded function than with the simple states linearization.

748

749 In contrast with the previous results, that serve only to evaluate the performance
750 of the methods, the MOO problem formulated based on the profit function J_2 , the
751 energy consumption J_3 and the distillate quality J_4 serves to critically evaluate op-
752 timal operational conditions for the debutanizer column. The results via ESO and
753 black box approach corresponding to this MOO problem are presented in Figure
754 11. In this case it was decided to impose the problem's inequality constraint ex-
755 plicitly in the optimization problem formulation for the black box approach. Thus
756 both approaches are implemented in the same way in order to be compared. As
757 expected since no design specification are set in Aspen Plus, the black box opti-
758 mization produces a set of Pareto solutions (black circles (o)) that is spread over
759 the Pareto front. However the solution via the ESO approach remains more infor-
760 mative because of the even distribution of the Pareto points. Additionally, many
761 of the optimal solutions obtained via black box optimization are out of the region
762 between individual minima, some of the solutions present small violations of the
763 quality constraint and the three anchor points are not part of the solution. Re-

garding computational performance, the results presented in Figure 11 comprise 45 points in both cases and its convergence required 2.61 and 2.65 minutes for ESO and black box approach respectively. In this case both optimization approaches offer equivalent computational performance, therefore the ESO approach should be preferred because of the better quality of the results.

From the results in Figure 11 the conflictive character of the three objectives is clear. Even though the profit function (Equation 9) depends on both terms, i.e., distillate quality and energy consumption, the behavior of none of them is fully correlated to the profit function. From these results it is interesting to see how the maximum profit results from having a low quality distillate ($> 4\% C_5$), these can be attributed to the fact that for those conditions higher quality is achieved for the bottom product, which influences the profit function more because of its linear increase on price and the higher productivity. Additionally, this result is achieved at a lower energy demand than if high quality were desired for both top and bottom products. In terms of sensitivity analysis or the opportunity cost the Pareto front presents what would be interesting regions for a decision maker. The region of optimal solutions close to the maximum profit shows how lowering the profit on small proportions can generate significant reductions on energy demand and improvements on the quality of the product. An interesting tradeoff for the decision maker would be to evaluate the solutions with a high quality distillate ($< 4\% C_5$) to see how the profit and energy demand are affected. This is for instance a distillate with 3.9 % C_5 can be obtained with 11.4 MW less energy demanded and only a reduction of 4.2 % in the profit for the operation. The later profit reduction is due to the reduction on the quality of the bottom product. An alternative approach to reflect the value of the information provided on the Pareto front is the ease on evaluating the opportunity cost for certain decisions, e.g., if the energy provided to the process is reduced or limited the impact can be rapidly determined and new operational conditions established to guarantee the best possible outcome.

5.2. Butyl acetate production

Two different MOO problems were evaluated for this case study. As common objective functions, the total energy demanded (J_1) and the recycle flow (J_2) in the

process were minimized. The benefit obtained by any improvement in the former objective is clear while for the latter, an indirect improvement of the process is expected. The reduction of inventories circulating in the process, which directly implies the reduction in size of equipments, pipelines and accessories (e.g., valves and fittings) is one of these positive effects. The first MOO optimization problem is completed with the quality of the methanol produced as by-product as third objective function (J_3). For the original process a benchmark of purity $> 92.8\%$ is specified. This quality specification is traditionally sufficient since the product is recycled to the PVA production. However, the tradeoff between a higher quality of this product and the energy demand might result in a more valuable outcome. The second MOO problem formulated for this case study replaces the quality objective function by a profit-cost function (J_4). As in the first case study including this objective results in a more realistic application of the proposed interface on a practical-industrially relevant case.

The first objective function corresponding to energy consumption is given in Equation (12a). The total recycle flow is expressed as the summation of the two distillate streams from columns C2 and C3 which are totally recycled in the process. Equation (12b) denotes this objective function. For the quality of the methanol product stream the formulation is given in Equation (12c), and it corresponds to the maximization of the molar fraction of methanol in the product stream from column C2. Finally the profit-cost function is presented in Equation (13). To determine the profit over the process operation, the sales of the two products i.e., butyl acetate and methanol are considered as income. A fixed price is considered for the butyl acetate, since it is accepted only at the quality standards. In contrast methanol has only a lower quality bound and a higher purity is technically feasible. Therefore the value of any improvement in the methanol quality is weighted through a price function. Similar to the profit function for the debutanizer, a logistic function was used to establish price levels depending on the product quality. In this case the methanol was evaluated at three different quality conditions, a low quality product ($> 92.8\% CH_3OH$), a medium quality ($> 98.5\% CH_3OH$) and a high quality product ($> 99.5\% CH_3OH$). The operational costs result from the needed energy

and the feedstock. Value is only assigned to the butanol stream, because as explained before the input stream containing methyl acetate is a side stream from the PVA process. In Equation (14) the mathematical formulation of the complete optimization problem is presented.

$$J_1 = \sum_{i=1}^{15} |x_i| \quad [MW] \quad (12a)$$

$$J_2 = x_{18} + x_{19} \quad [kmol/s] \quad (12b)$$

$$J_3 = -x_{16} \quad [mole.frac.] \quad (12c)$$

$$\begin{aligned} J_4 &= -(\text{income} - \text{costs}) \quad [\$ / h] \\ \text{income} &= a_1 x_{21} + \left(\frac{a_2}{1 + e^{(-a_3(x_{16} - a_4))}} + \frac{a_5}{1 + e^{(-a_6(x_{16} - a_7))}} + a_8 \right) x_{20} \\ \text{costs} &= a_9 x_{22} + 3600 \times a_{10} (-x_2 - x_3 - x_6 - x_{11} - x_{13}) + \\ &\quad 3600 \times a_{11} (x_8 + x_{14} + x_{15}) + a_{11} (x_1 + x_4 + x_5 + x_7 + x_9 + x_{10} + x_{12}) \\ a_1 &= 0.9000 \quad a_4 = 0.9935 \quad a_7 = 0.9790 \quad a_{10} = 1.0 \times 10^{-10} \\ a_2 &= 0.30 \quad a_5 = 0.20 \quad a_8 = 0.20 \quad a_{11} = 9.0 \times 10^{-5} \\ a_3 &= 6000 \quad a_6 = 600 \quad a_9 = 0.60 \quad a_{12} = 8.98 \times 10^{-9} \end{aligned} \quad (13)$$

$$\begin{aligned} \min_{\mathbf{u} \in R^6} \quad & [J_1, J_2, J_3] \\ \text{s.t.:} \quad & g_1(x) : 0.928 - x_{16} \leq 0 \\ & g_2(x) : 0.995 - x_{17} \leq 0 \\ & 0.24 < u_1 < 0.4 \quad 0.55 < u_2 < 0.62 \\ & 0.75 < u_3 < 1.2 \quad 0.5 < u_4 < 0.7 \\ & 1.87 < u_5 < 2.5 \quad 0.65 < u_6 < 0.75 \end{aligned} \quad (14)$$

In Figure 12 the optimal results are depicted for both optimization problems. Figure 12a corresponds to the methanol quality-based Pareto front, while Figure 12b presents the results for the profit-based MOO optimization. In both cases the solution is presented with reference to the original process conditions (+). From Figure 12 the optimization potential of the process becomes clear. Hence, these

839 results can be studied to evaluate the advantages that each individual optimal con-
 840 dition offers and the possible tradeoffs between them. The optimal solutions for the
 841 four objectives are presented in Table 11, together with the reference condition of
 842 the original process (Luyben, 2011). The optimal solution for the energy demand
 843 (J_1) results in a reduction of 2.214 [MW] which is a reduction of 9.94%. If the the
 844 recycle flows are minimized (J_2), a total reduction of 0.0239 [kmol/s] is achieved,
 845 this is equivalent to 29.2% less than the original total recycle flow. From these indi-
 846 vidual minima it is interesting to see that contrary to what can be expected, having
 847 the maximum reflux ratio in the columns does not necessary imply the highest total
 848 energy demand. This is explained by the fact that by increasing the reflux ratio, a
 849 higher purity is obtained on the top products which in turn are recycled to the reac-
 850 tor section with lower contents of the product substances. This means shifting the
 851 reaction equilibrium towards the products which in turn drives to higher conversion
 852 and then at the end less material have to be processed by the distillation train. For
 853 this specific result, the energy demand is even lower than in the original process
 854 (21.419 vs. 22.284 [MW]). Furthermore, the corresponding distillate to feed ratios
 855 in each column can be seen as the adjusted variable to meet the quality constraints.

856
 857 In the case of maximizing the methanol quality (J_3) the molar concentration of
 858 methanol in the product stream (bottom of the C2-column) increases from the
 859 benchmark value, 92.8% to 99.6%. This improvement brings the product quality
 860 closer to the commercial grade for methanol. To achieve this optimal condition, the
 861 controls are varied to a new condition that favors the purification of methanol. As
 862 it can be seen in Table 11, it is the optimal condition with the highest distillate to
 863 feed ratio (u_4) and a relatively low reflux ratio (u_3) in column C_2 . This explains
 864 the high purity on the bottom stream (methanol), but it also implies larger flow
 865 and lower quality for the distillate, which goes against the conditions identified for
 866 low energy demand. In fact, this optimal condition implies the highest total energy
 867 demand and total recycle flow from the possible solutions. Finally the conditions
 868 for maximum profit (J_4) are similar to those achieved for maximum methanol qual-
 869 ity. However, the methanol quality is slightly lower, being sufficient to achieve the
 870 maximum value of the logistic price function. The consumed energy is significantly

less not only due to the reduction of the methanol quality but because of the explicit inclusion of the energy cost in the objective function. The optimal solution for the profit function is in fact a specific tradeoff point between quality and energy. This can be seen when comparing the two Pareto fronts in Figure 12. The individual maximum for the profit function corresponds to a Pareto point in the valley region close to the optimal methanol quality in Figure 12a. The optimal values for the independent variables show that one of the reasons for maximum profit is a lower distillate to feed ratio (u_4) in column C_2 than for the optimal quality, being this a reason as well for the lower energy demand compare to the maximum methanol quality.

Regarding different tradeoff solutions for the butyl acetate process, in Figure 12 the obtained Pareto fronts present steep regions between, on the one hand, the energy and recycle anchor points and on the other hand, the quality of methanol or the profit. In case of Figure 12a, it is only after high quality values are reached (mole fraction > 0.985) that a pronounced change on direction is seen, making any further increase on quality highly expensive in terms of energy demand, with a fast increase on the required recycle and therefore with a less significant gain on the profit. This can be considered as a favorable property in case the desired tradeoff between these objectives is to have a significant increase in methanol purity and therefore profit but keeping energy demand and recycle flow below the original process values. One possible solution corresponds to the optimal solution having 99.4mole% of methanol purity and the minimum energy demand. Thus for this solution the energy demand would be 21.1925 [MW] and the recycle flow 0.066 [kmol/s]. This solution represents a tradeoff where 97% of the potential improvement on quality is achieved while 49% and 66% of their potentials reductions are achieved for energy demand and recycle flow. The maximum potential of improvement for each objective function corresponds to pass from the original process condition to each individual optimal solution. Other optimal solutions can be chosen depending on the decision maker's preferences or criteria. From Figure 12b it is interesting to see that this Pareto front has a combination of concave and convex regions, which are attributed mainly to the steps on the price function for methanol. Additionally the region towards

903 the border of minimum energy in the Pareto front shows a very particular behavior.
904 Since the improvement on methanol quality is restricted due to the condition of low
905 energy demand, the profit is kept relatively low till the point when the limitation is
906 overcome and a very sharp increase in profit is produce due to the sudden increase
907 in methanol quality.

908

909 Regarding convergence of the series of parametric SOOPs (the tradeoff points of in-
910 terest) issues occurred when the NBI method was applied. It is considered that the
911 noise introduced by the convergence error tolerance in Aspen Plus affects the solu-
912 tion of the parametric subproblems more than the original single objective problems,
913 this convergence issue is discussed as well by Jang et al. (2005). Therefore, since
914 the NBI method transforms the three objective functions into equality constraints
915 to formulate the parametric single objectives, the problem becomes more complex
916 and sensitive to be affected by noise. Hence the NNC method is used as alterna-
917 tive. Since this method is based on the same principle applied by the ε -constraint
918 method, the resulting parametric formulation does not depend on modifying and
919 combining the objective functions and therefore is assumed to be less prone to the
920 same issues experienced with NBI.

921

922 In order to prevent or reduce the possible negative effect of noise propagation from
923 the inexact convergence of Aspen Plus to the NLP solver some aspects can be con-
924 sidered when modeling the process, formulating and solving the NLP problem. The
925 equation oriented mode of Aspen Plus offers several parameters to configure its
926 internal NLP solver, e.g., method applied, tolerances, number of iterations. These
927 features can be adjusted to reduce as much as possible the residual value after
928 convergence ($\mathbf{R}$) and therefore to have more accurate solutions for the states and
929 Jacobian. However imposing tight conditions (e.g., very low tolerances) can turn
930 the model unstable reducing convergence robustness and making the optimization
931 parsimonious. In case the process model contains non supported units for analytical
932 derivation in the EO mode, the perturbation size for the numerical derivation that
933 is applied in Aspen Plus, can be adjusted to find and equilibrium between error in
934 the approximation and convergence noise. Navarro-Amoros et al. (2014) discusses

935 how to reduce the noise amplification due to recycles in the flowsheet. The system
936 can be modeled with open recycles so the simulator does not have to converge for
937 those streams. This task is transferred to the external NLP solver. Even though
938 the optimization problem becomes larger (i.e., more variables and explicit equality
939 constraints) the use of the explicit solver makes the solution more robust, less prone
940 to noise and the computational time was found to be similar. Finally, as observed
941 in this contribution for MOO the NNC method should be preferred over the NBI. In
942 general, methods that do not require adding explicit nonlinear equality constraints
943 should be preferred.

944

945 Through preliminary evaluations it was found that higher convergence robustness
946 can be given to the model in Aspen Plus if additional constraints are set to the
947 optimization problem in order to avoid unfeasible conditions for the solver in Aspen
948 Plus. Specifically for the butyl acetate production process it was found that for
949 the region with high methanol quality and low energy the NLP solver pushes the
950 independent variables of the first distillation column (C1 reflux u_1 and distillate to
951 feed u_2 ratios) to values that result in no liquid and/or vapor flow at certain stages
952 in the column. Therefore resulting in major errors for the convergence in Aspen.
953 Based on the preliminary results it was concluded that since the mass balances are
954 not explicitly constraints for the optimization solver, and since in the original prob-
955 lem formulation there exist no constraint over any condition of the column C1, the
956 solver tries to set the conditions of the tower towards a perfect separation of the
957 mixtures MeAc/MeOH in the top and BuAc/BuOH in the bottom product. This
958 condition drives the simulation very close to an infeasible region for convergence. To
959 reduce this effect it was decided to impose two additional constraints on a minimum
960 concentration (traces) of these products on the respective streams so the conditions
961 of the column are kept in a feasible region.

962

963 5.3. Methanol production

964 For this process three objective functions were optimized, i.e., the carbon effi-
965 ciency, total energy consumption and the profit. First, since the main purpose of
966 this process is to treat the CO_2 present on the flue gas from combustion processes

(e.g. from electric power plants or thermal installations) and to produce an added value product, the carbon efficiency is critical to determine the extent of effectiveness of the process. The carbon efficiency is formulated as the ratio between carbon atoms that are converted to the added value product (i.e. CH_3OH) and the carbon atoms from the carbon source (i.e. CO_2 and CH_4). In Equation (15a) this objective is formulated as the ratio between the molar flow of these substances in the inlet streams and the top product of the distillation column. Other methanol molecules present in side streams (e.g. purge) as well as the unreacted material are considered losses. The second objective function evaluates the total energy demand per kmol of methanol produced, as established in Equation (15b).

Finally, the third objective function is a profit-cost function. This objective considers the income based on the methanol sales and the operational cost due to feedstock and the energy consumed. Additionally in this case the annualized capital cost (ann.CC) of the main units is considered since the operational conditions will determine the size and design requirements of these units. This objective is formulated according to Equation (16). Quality is not considered in this case as a parameter to define the product selling price. The product price is fixed based on its compliance with the quality specification, as it is established in the first constraint (Equation 17). The feedstock and energy costs are presented in Table 8, these values are taken from Zhang et al. (2013). The ann.CC is determined from the total capital cost (Total.CC) as described by Navarro-Amoros et al. (2014) considering a time horizon (n) of 10 years and an interest rate per year (i) of 8 %. To evaluate the capital cost only a subset of the units are considered. They are: compressors, methanol reactor and flash vessels. These units are considered as main contributors to the capital cost and these will be directly affected by the operational conditions evaluated in the optimization problem. The tri-reforming reactor is considered as well a main contribution to the capital cost of the process, however in this case a fixed capital cost is assumed since, contrary to the methanol reactor, the favorable conditions for kinetics and equilibrium of the tri-reforming process are both achieved at high temperatures. Moreover since it is a very fast reaction in the range of temperatures to be evaluated it can be assumed that the most favorable

999 conditions are governed by the reaction equilibrium. The boundaries established
 1000 for the independent variables and the constraints on the optimization problem are
 1001 formulated in Equation 17. The first three constraints guarantee a correct set of
 1002 pressures in the process, with successively lower pressure for the two separators and
 1003 the distillation column. The other two constraints set quality conditions for the
 1004 products, i.e, methanol and water (diluted methanol).

$$J_1 = - \left(\frac{x_2}{u_1 + x_1} \right) \quad (15a)$$

$$J_2 = \frac{\sum_{i=5}^{19} |x_i|}{x_2/3600} \quad [MJ/kmol] \quad (15b)$$

1005

$$J_3 = - \left(\text{income} - \text{costs} - \frac{\text{ann.cc}}{8000} \right) \quad [$/h]$$

$$\text{income} = a_1 x_2$$

$$\text{costs} = a_2 u_1 + 3600 \times a_3 (-x_{11} - x_{12} - x_{14} - x_{15} - x_{16} - x_{18}) +$$

$$3600 \times a_4 (x_5 + x_7 + x_8 + x_9 + x_{19}) + a_5 (x_6 + x_{17} + x_{13}) \quad (16)$$

$$\text{ann.CC} = (\text{Total.CC}) \frac{i * (1 + i)^n}{(1 + i)^n - 1}; \quad i = 0.08 \quad n = 10$$

$$a_1 = 0.80 \quad a_3 = 1 \times 10^{-10} \quad a_5 = 8.98 \times 10^{-9}$$

$$a_2 = 0.50 \quad a_4 = 9 \times 10^{-5}$$

1006

$$\min_{\mathbf{u} \in R^6} [J_1, J_2, J_3]$$

$$\text{s.t.: } g_1(u) : 0 < u_6 - u_9 \leq 70 \quad g_2(u) : 0 < u_9 - u_{10} \leq 25$$

$$g_3(u) : u_{13} - u_4 = 0 \quad g_4(x) : 0.993 - x_3 \leq 0 \quad g_5(x) : x_4 - 0.85 \leq 0$$

$$200 < u_1 < 800 \quad 1 < u_2 < 5 \quad 400 < u_3 < 980$$

$$50 < u_4, u_{13} < 300 \quad 200 < u_5 < 300 \quad 25 < u_6 < 40$$

$$25 < u_7 < 50 \quad 0.05 < u_8 < 0.3 \quad 9 < u_9 < 30$$

$$9 < u_{10} < 30 \quad 1.5 < u_{11} < 3 \quad 0.95 < u_{12} < 0.988$$

(17)

1007 In Figure 13 the optimization results are depicted. In this case the reference
 1008 conditions (+) are the optimal values reported for the same process by Zhang et al.
 1009 (2013). As in the previous case studies the results of the MOO immediately point

1010 out the potential process improvement compare to reference conditions, and there-
1011 fore the significant added value of applying this optimization strategy. The numer-
1012 ical optimal solutions for the three objectives are presented in Table 13, together
1013 with the reference condition of the original process (Zhang et al., 2013). Regarding
1014 individual optimal solutions, the process shows a theoretical high potential to signif-
1015 icantly improve the carbon efficiency obtained with the reference conditions. With
1016 a carbon efficiency of 96 %, this process has a enormous environmental potential.
1017 However apart from the optimal conditions in the methanol reactor and the process
1018 loop, the most significant contribution to achieve the high carbon efficiency is the
1019 use of an almost stoichiometric amount of methane for the tri-reforming. From a
1020 practical point of view these conditions can be undesired because they demand a
1021 very accurate control of the reactor conditions to guarantee the highest possible
1022 conversion of CO_2 . In practice an small excess of methane could be fed into the
1023 reactor to guarantee the desired conversion. The profit (J_3) was maximized, reach-
1024 ing the highest value of 4733.5 [\$/h] of economical benefit. However it has to be
1025 considered that a real value should be significantly lower due to the capital costs
1026 that were not considered because of their approximated constant character. Finally
1027 regarding energy, the minimum energy demand required by the process (J_2) is cal-
1028 culated to be 994.9 [MJ/kmol], which means a reduction of 26.6 % (360 [MJ/kmol]).
1029
1030 Similarly to what was found for the butyl acetate case, the convergence for this
1031 MOOP was obtained using NNC as scalarization method and two additional con-
1032 straints were added to guarantee robustness for the model convergence in Aspen
1033 Plus. These constraints do not have a physical interpretation but help to avoid
1034 conditions that result on simulation errors in Aspen Plus. In this case, through
1035 preliminary studies, the distillation column was found as the most prone unit to
1036 generate errors. Therefore constraints were added to guarantee a minimum concen-
1037 tration of the trace components in both distillate and bottom products.
1038
1039 Finally, the detailed inspection of the Pareto front in Figure 13 shows that the
1040 system has a strong convex behavior on the Pareto front. In turn there exist
1041 strongly advantageous solutions that a decision maker could choose. Similar to

the profit-based MOO optimization for the butyl acetate case, the Pareto front shows a particular shape on the side of tradeoff points with minimum energy demand. Since these solutions are limited by a low energy consumption, they offer a moderate improvement on the carbon efficiency compare to the one obtained at the opposite side of the Pareto front. Therefore, starting from the points of minimum energy demand and maximum profit, there is a preferential path for rapidly increase on the carbon efficiency till a value around 93 % is achieved. This implies that there exist a region with tradeoff solutions that offer a significant improvement on the carbon efficiency keeping a relatively low energy demand and a high profit. One possible optimal solution in this region would be the one corresponding to 93.17 % carbon efficiency, 1033.8 [MJ/kmol] required energy and a profit estimated of 4024.2 [\$/h]. This solution is significantly better than the reference conditions regarding the three objectives simultaneously, and it represents an improvement of 85.6, 89.2 and 63.8 % of the maximum potential improvement for each objective.

Regarding computational performance of the latter case studies, in Table 14 the computational time for each case study applying the developed gradient-based optimization interface is reported. All problems were solved with a laptop computer featuring an Intel $\text{\textcircled{R}}Core^{TM}$ i7-4500U at 2.40 GHz and 8 GB of RAM. The table shows the problem scale in each case. The scale is given by the model's size (i.e., in Aspen Plus the number of equations/dependent variables and number of independent variables), and the scale of the optimization problem which considers the number of degrees of freedom (i.e., a sub set of the independent variables in Aspen Plus) and the number of constraints. The number of Pareto points produced in the solution is taken into account to determine the average time spent per optimal point as an indicator of the computational performance. Even though the scale of the methanol case study is smaller in terms of number of equations in the simulation, the computational performance is slower. With 86.4 seconds per Pareto point it takes around three times longer than the butyl acetate case. This difference can be attributed to the model and optimization complexity. Even though the solution of the methanol case requires the convergence of less equations, it takes longer to the EO solver to find a solution. This is attributed to the system complexity which

1074 includes two reactors, one of which depends on the total Gibbs free energy mini-
1075 mization algorithm of Aspen Plus. Additionally, the higher number of degrees of
1076 freedom results in a larger optimization problem, possibly with a higher compu-
1077 tational effort if the constraints are highly nonlinear. Evidence of these elements
1078 can be found in the results reported by IPOPT regarding the time spent evaluating
1079 the objective functions and constraints (where the time required by Aspen Plus to
1080 converge is the major contributor) and the number of evaluations of these functions.
1081 While for the butyl acetate case the average time per evaluation is the 1.3 s, for
1082 the methanol case is 1.9 s. This clearly demonstrates the higher complexity for
1083 simulating the latter case study. Moreover, finding one Pareto point for the butyl
1084 acetate case required in average 13 evaluations while for the methanol case 37 were
1085 needed in average. This corresponding to the higher scale of the latter optimization
1086 problem.

1087

1088 These results demonstrate the key role that the model complexity in Aspen Plus
1089 plays for the computational performance of the optimization interface. Therefore
1090 it is difficult to establish the limiting scale for which the solution of the optimiza-
1091 tion problems becomes infeasible using the developed interface. Even for very large
1092 optimization problems with many degrees of freedom and constraints, results in
1093 acceptable computational time can be achieved if the model complexity in Aspen
1094 Plus is sufficiently low. This is possible due to the robustness of the CasADi -
1095 IPOPT framework. As an illustration of the computational efficiency of CasADi,
1096 Vallerio et al. (2016) have reported convergence time around 19 minutes for large
1097 scale dynamic optimization problems with 30 states 52,272 variables and 123,552
1098 constraints.

1099 6. Conclusion

1100 Aspen and CasADi have been selected as the tools for computer-aided engi-
1101 neering in order to enable MOO in a flowsheet simulator. Two interfaces have been
1102 successfully constructed. The first one corresponds to approaches for *black box opti-*
1103 *mization* while the second one *accesses the ESO*. The former, based on vectorization
1104 methods, corresponds with the scheme that has been most commonly exploited in

1105 the current state-of-art. It has been implemented to generate reference results for
1106 the first case study. The latter interface, based on scalarization methods is the main
1107 contribution of this paper. In addition the specific challenges of interfacing process
1108 simulators with optimization tools have been highlighted. The presented novel im-
1109 plementation allows gradient-based MOO of processes simulated with Aspen Plus,
1110 benefiting from the gradient information produced by the Aspen's EO engine.

1111

1112 Exploiting the gradient-based optimization results in a higher accuracy of the Pareto
1113 front and better capabilities to tackle constrained problems. Using the debutanizer
1114 column as a very intuitive case study with an illustrative objective function and a
1115 more realistic profit function, it has been possible to demonstrate the higher per-
1116 formance of this optimization approach. On the one hand, it demands, in the worse
1117 case similar computational time to the black box optimization, since fewer evalu-
1118 ations of the objective functions are required. And on the other hand it produces
1119 always more accurate and informative optimal solutions that serve to approximate
1120 the complete Pareto front. In terms of limitations of the developed optimization
1121 interface, these can be subdivided into two groups. On the one hand, some aspects
1122 are inherent to the MOO methods applied. This is illustrated in the debutanizer
1123 case study with the possibility of obtaining non-global optimal solutions and the
1124 tendency to produce non-optimal Pareto solutions. On the other hand, related di-
1125 rectly to the architecture of the interface, the fact that the optimization accessing
1126 the ESO relies on a bi-level optimization scheme, where the system of flowsheet
1127 model equations is solved independently while in the upper level the MOO problem
1128 is solved based on those results, introduces uncertainty into the problem. Even
1129 though this limitation was surpassed in this contribution using NNC instead of NBI
1130 as scalarization method, this aspect could represent problems for other applications.

1131

1132 The developed tools have been illustrated with three relevant case studies, i.e.,
1133 the debutanizer column, the butyl acetate process and the methanol production via
1134 tri-reforming. In all cases the Pareto front obtained proved to be very informative,
1135 providing beneficial tradeoffs for the optimization of each process. Specifically in the
1136 butyl acetate and methanol case studies, significant improvements with respect to

the current reference operating conditions have been observed. These results show that interfacing a process simulator for MOO can provide the process engineer with a better insight into the process conditions, while providing more alternatives to the decision maker. In future work the goal is to integrate the presented interface with interactive methods as discussed by Vallerio et al. (2015).

Acknowledgments

This work was supported by KU Leuven PFV/10/002 Center-of-Excellence Optimization in Engineering (OPTEC), CAM holds a VLAIO-Baekeland [HBC.2017.0239] grant, Fonds Wetenschappelijk Onderzoek Vlaanderen [G.0930.13] and the Belgian Science Policy Office (DYSCO) [IAP VII/19].

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1317 **Tables**

Compound/Fraction	wt%
Propene (225.55 K)	1.2
Propane (230.95 K)	3.2
Isobutane (260.15 K)	0.5
Butane (272.15 K)	2.3
Butenes (266.68 K)	1.8
C_5 - 453.15 K	81.8
453.15 K - 623.15 K	9.2

Table 1: Feed composition for the debutanizer column.

Parameter	Value	Units
Feed Temperature	441.15	K
Feed Pressure	1.52	MPa
Feed Mass Flow	38.3	kg/s
Number of stages	16	-
Feed stage	7	-
Pressure at condenser	1.1	MPa
Degrees subcooled	288.15	K

Table 2: Process conditions and fixed parameters for the debutanizer column optimization.

Variable	Optimization	Simulation	Units
Controls	u_1	Mass reflux ratio	-
	u_2	Distillate mass flow	kg/s
States	x_1	Reboiler duty	MW
	x_2	Condenser duty	MW
	x_3	C_5 wt fraction in distillate	-
	x_4	Bottoms mass flow	kg/s
	x_5	Isobutane wt fraction in bottoms	-
	x_6	Butane wt fraction in bottoms	-
	x_7	Butene wt fraction in bottoms	-
	x_8	Feed mass flow	kg/s

Table 3: Description of the model states and control variables for the debutanizer.

	Parameter	Value	Units
Feed 1 (MeAc)	Pressure	1.013	MPa
	Temperature	305	K
	Flow	100	kmol/h
	MeAc	0.6	Mole-frac.
	MeOH	0.4	Mole-frac.
Feed 2 (BuOH)	Pressure	1.013	MPa
	Temperature	305	K
	Flow	59.4	kmol/h
	BuOH	1.0	Mole-frac.
Reactor	Temperature	350	K
C1	Num. stages	37	-
	Cond. Pressure	0.122	MPa
C2	Num. stages	27	-
	Cond. Pressure	0.111	MPa
C3	Num. stages	47	-
	Cond. Pressure	0.405	MPa

Table 4: Process conditions and fixed parameters to model and optimize the butyl acetate production process.

Variable	Optimization	Simulation	Units
Controls	u_1	Reflux ratio C1	-
	u_2	Distillate to feed ratio C1	-
	u_3	Reflux ratio C2	-
	u_4	Distillate to feed ratio C2	-
	u_5	Reflux ratio C3	-
	u_6	Distillate to feed ratio C3	-
States	x_1	B4 Heat duty	MW
	x_2	B5 Cooling duty	MW
	x_3	CSTR Cooling duty	MW
	x_4	B10 Heat duty	MW
	x_5	C1 Reboiler duty	MW
	x_6	C1 Condenser duty	MW
	x_7	B11 Heat duty	MW
	x_8	P9 Work duty	MW
	x_9	B12 Heat duty	MW
	x_{10}	C2 Reboiler duty	MW
	x_{11}	C2 Condenser duty	MW
	x_{12}	C3 Reboiler duty	MW
	x_{13}	C3 Condenser duty	MW
	x_{14}	P6 Work duty	MW
	x_{15}	P3 Work duty	MW
	x_{16}	Methanol purity (B2)	Mole frac.
	x_{17}	Butyl acetate purity (B3)	Mole frac.
	x_{18}	Molar flow distillate C2	kmol/s
	x_{19}	Molar flow distillate C3	kmol/s
	x_{20}	Mass flow methanol produced	kg/h
	x_{21}	Mass flow butyl acetate produced	kg/h
	x_{22}	Mass flow butanol (inlet)	kg/h

Table 5: Optimization variables designation for MOO of the butyl acetate process.

Parameter		Value	Units
CH4	Pressure	0.101	MPa
	Temperature	298.15	K
	CH_4	1.0	Mole-frac.
Fluegas	Pressure	0.101	MPa
	Temperature	423.15	K
	Flow	1000	kmol/h
	CO_2	0.1	Mole-frac.
	O_2	0.03	Mole-frac.
	N_2	0.67	Mole-frac.
	H_2O	0.2	Mole-frac.
Dist. Column	Num. stages	19	-

Table 6: Process conditions and fixed parameters to model and optimize the methanol production process.

Variable	Optimization	Simulation	Units
Controls	u_1	Methane molar flow (inlet)	kmol/h
	u_2	Pressure reforming reactor	MPa
	u_3	Temperature reforming reactor	K
	u_4	Pressure methanol reactor	MPa
	u_5	Temperature methanol reactor	K
	u_6	Pressure Separator 1	MPa
	u_7	Temperature Separator 1	K
	u_8	Purge fraction	-
	u_9	Pressure Separator 2	MPa
	u_{10}	Pressure dist. column	MPa
	u_{11}	Reflux ratio dist. column	-
	u_{12}	Distillate - feed ratio dist. column	-
	u_{13}	Discharge pressure recycle compressor	MPa
States	x_1	CO_2 molar flow (fluegas)	kmol/h
	x_2	CH_4O flow (methanol)	kmol/h
	x_3	CH_4O purity (methanol)	Mole-frac.
	x_4	CH_4O fraction (water)	Mole-frac.
	x_5	In-pre work duty	MW
	x_6	H-1 Heat duty	MW
	x_7	Press-1 work duty	MW
	x_8	Press-2 work duty	MW
	x_9	Press-3 work duty	MW
	x_{10}	H-2 Heat duty	MW
	x_{11}	C-2 Heat duty	MW
	x_{12}	Dist. condenser duty	MW
	x_{13}	Dist. reboiler duty	MW
	x_{14}	C-1 Heat duty	MW
	x_{15}	C1 Heat duty	MW
	x_{16}	C2 Heat duty	MW
	x_{17}	Reforming reactor heat duty	MW
	x_{18}	Methanol reactor heat duty	MW
	x_{19}	Recycle comp. work duty	MW
	x_{20}	CO conc. MeOH reactor	Mole frac.
	x_{21}	CO_2 conc. MeOH reactor	Mole frac.
	x_{22}	H_2 conc. MeOH reactor	Mole frac.
	x_{23}	H_2O conc. MeOH reactor	Mole frac.
	x_{24}	CH_4O conc. MeOH reactor	Mole frac.
	x_{25}	Equilibrium constant RX Eq.7a	-
	x_{26}	Equilibrium constant RX Eq.7b	-
	x_{27}	H_2 converted MeOH reactor	kmol/h
	x_{28}	Actual vol. gas flow Separator 1	m^3/h
	x_{29}	Actual vol. gas flow Separator 2	m^3/h

Table 7: Optimization variables designation for MOO of the methanol process.

	Item	Specification	Price
Chemicals	Methanol	≥ 99.5 wt % pure	0.8 (\$/kg)
	Methane	≥ 99 mol % pure	0.5 (\$/kg)
Utilities	Cooling water	4,184 J/kg	0.1 (\$/GJ)
	Electricity	-	0.09(\$/kWhr)
	Heat	55,688 kJ/kg	0.5 (\$/kg)

Table 8: Chemicals and utilities prices for profit evaluation

Results	Optimization accessing ESO		Black box optimization
	States linearization	Embedded state function	
Convergence time [min]	0.61	0.72	1.35
Controls u_1	23.88	23.85	21.95
u_2	10679	10679	10640
Objective function	-557.76	-557.71	-497.39
Constraint	0	0	$1.69 \cdot 10^{-4}$

Table 9: Results for the optimization of the illustrative objective function for the debutanizer column, subject to the quality constraint.

Convergence time [min]	Optimization accessing ESO		Black box optimization
	States linearization	Embedded state function	
Bi-objective 16 Pareto points	2.99	3.73	3.47
Tri-objective 45 Pareto points	9.38	10.51	2.41

Table 10: Convergence time for bi and tri objective optimization problems for the debutanizer column using the illustrative function.

Results		Total energy demand minimized	Total recycle flow minimized	Methanol quality maximized	Profit maximized	Original process Luyben (2011)	
Controls	u_1	0.2400	0.2968	0.3793	0.3149	0.3170	-
	u_2	0.5883	0.5739	0.5904	0.5915	0.6119	-
	u_3	1.0758	1.2000	1.0542	0.9820	0.9960	-
	u_4	0.5407	0.5000	0.6333	0.6021	0.6199	-
	u_5	2.6971	3.8000	2.4588	2.5304	1.9200	-
	u_6	0.6657	0.6560	0.6842	0.6562	0.6946	-
Objective functions	J_1	20.0699	21.4196	24.3717	21.7163	22.2840	MW
	J_2	0.0643	0.0579	0.0838	0.0735	0.0818	kmol/s
	J_3	-0.9280	-0.9280	-0.9960	-0.9951	-0.9284	(-)mole frac.
	J_4	-3411	-3398	-5419	-5463	-3375	(-)\$/h

Table 11: Results for the multi-objective optimization of the butyl acetate production process.

IPOPT options	Debutanizer			
	Illustrative case	Profit MOO	Butyl Acetate	Methanol
Convergence tol.	1×10^{-5}	def.	1×10^{-5}	1×10^{-5}
Dual infeasibility tol.	def.	def.	1.5	1×10^{-5}
Constraint violation tol.	def.	def.	1×10^{-3}	1×10^{-5}
Complementarity tol.	def.	def.	1×10^{-3}	1×10^{-5}
Acceptable iter.	5	def.	3	3
Accep. convergence tol.	0.05	def.	0.5/5	5×10^{-3}
Accep. dual inf. tol.	0.05	def.	0.5/5	5×10^{-3}
Accep. constraint vio. tol.	1×10^{-3}	def.	5×10^{-3}	1×10^{-4}
Accep. Complementarity tol.	1×10^{-2}	def.	1×10^{-4}	1×10^{-4}
Accep Obj. change tol.	1×10^{-3}	def.	5×10^{-3}	5×10^{-2}
Hessian approximation		limited-memory		
Linear solver		MUMPS		
Pivot tolerance		default: 1e-6		

Table 12: IPOPT options used for the solution of the case studies.

Results		Carbon effic. maximized	Total energy demand minimized	Profit maximized	Original process Zhang et al. (2013)	
Controls	u_1	345.93	378.80	365.19	400.00	kmol/h
	u_2	1.0000	3.7428	2.1283	1.0000	MPa
	u_3	980.00	942.96	980.00	850.00	K
	u_4	300.00	173.76	50.000	50.000	MPa
	u_5	200.00	200.00	200.00	220.00	K
	u_6	40.000	31.804	40.000	24.000	MPa
	u_7	25.000	31.617	25.000	25.000	K
	u_8	0.0500	0.3000	0.0500	0.0500	-
	u_9	9.1178	9.0000	12.750	10.000	MPa
	u_{10}	9.0000	9.0000	12.750	10.000	MPa
	u_{11}	3.0000	1.5000	1.5000	1.5000	-
	u_{12}	0.9880	0.9880	0.9888	0.9888	-
	u_{13}	300.00	173.76	50.000	50.000	MPa
Objective functions	J_1	-0.9604	-0.8483	-0.8693	-0.7617	(-effc.)
	J_2	1566.9	994.9	1150.5	1354.9	[MJ/kmol]
	J_3	-931.5	-4269.0	-4733.5	-2771.2	[(-)\$ /h].

Table 13: Results for the multi-objective optimization of the methanol production process.

MOO Problem		Problem scale				Number Pareto pints	Total time [min]	Time per Pareto point [min]
		Simulation # Eq.	Ind. var.	Optimization deg. of freedom	const.			
Butyl acetate	Quality-based	2919	169	6	6	28	13	0.46
	Profit-based	2919	169	6	6	28	14.4	0.52
Methanol via tri-reforming		1572	306	13	7	15	21.6	1.44

Table 14: Computational performance for the MOO of the butyl acetate and methanol processes.

1318 **Figures**

Figure 1: Concept of the interface architecture.

Figure 2: Scheme of the interface constructed for black box optimization exploiting a genetic algorithm in Matlab.

Figure 3: Scheme of the interface constructed for optimization accessing the ESO exploiting gradient-based optimization algorithms of CasADi for Matlab.

Figure 4: Debutanizer column with decision variables and model states.

Figure 6: Methanol production process via tri-reforming.

(a) Best known optimal solution for ESO approach.

(b) Local optimal solution for the ESO approach.

Figure 7: Convergence to different optimal points in a illustrative objective function - optimization accessing the ESO for the debutanizer column.

(a) Unsuccessful black box optimization.

(b) Black box optimization.

Figure 8: Convergence issues when problem must cope with constraints - black box optimization for the debutanizer column.

Figure 9: Comparison of the obtained Pareto front in the bi-objective optimization case for the debutanizer column.

Figure 10: Comparison of the Pareto front obtained via ESO approach (x) and black box optimization (black o) for the debutanizer column.

Figure 11: Pareto front for the profit-energy-quality optimization of the debutanizer column via ESO approach (x) and black box optimization (o).

(a) Quality-based MOO.

(b) Profit-based MOO.

Figure 12: Pareto front via ESO approach for MOO of the butyl acetate production process.

Figure 13: Pareto front via ESO approach for the carbon efficiency-energy-profit optimization of the methanol production via tri-reforming.