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Process intensification of reactive separator networks through the IDEAS conceptual framework

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ABSTRACT

A method to rigorously identify the performance limits of a reactive separator network is presented in this paper. The quantification of the enhancement potential for a given technology can greatly benefit process intensification studies in the pursuit of radical improvements. The Infinite DimEnsionAl State-Space (IDEAS) conceptual framework is first reviewed and then shown to be capable of assessing the potential for process intensification of reactive separation processes. The IDEAS framework is employed to formulate an infinite linear program (ILP) that can synthesize optimal reactive separation networks, and establish rigorous tradeoffs between total network reactive holdup, and total network capacity. The proposed reactive separation process intensification method is demonstrated on a case study involving the metathesis of 2-pentene through reactive distillation. Significant intensification over prior designs is demonstrated.

1. Introduction

Process intensification (PI) is a major focus of current chemical engineering research. The concept encompasses any chemical engineering development that offers drastic improvements in chemical processing, substantially decreasing equipment volume, energy consumption or waste formation (Stankiewicz and Moulijn 2000; Stankiewicz 2003). More recently, process intensification was presented as a set of principles that are applicable to a broader spectrum of disciplines (Van Gerven and Stankiewicz, 2009).

Process synthesis is the invention of chemical process designs to exploit chemical routes at the desired scale, safely, environmentally responsibly, efficiently, and economically in a manner superior to all other possible processes (Barnicki and Siirola 2004). Often referred as a process intensification example, design of reactive distillation systems has been pursued using process synthesis methods (Harmsen 2004). Nevertheless, most of the developments in process intensification are based on experimental work (Moulijn et al., 2008), and pilot plant facilities (Jan Harmsen 2007), while the development of a systematic approach for process intensification is still in its incipient stages (Baldea, 2015).

Considering this perspective, it is clear that PI can benefit from process synthesis tools that provide systematic approaches for design and optimization of intensified processes. Moreover, synthesis tools that enable the thorough identification of the performance limits for a particular technology is an indispensable PI development since it would establish metrics to quantitatively evaluate intensified processes.

The Infinite Dimensional Steady State (IDEAS) framework, a systematic approach for process synthesis, is applied in this work as a process intensification tool. IDEAS can rigorously identify the performance limits of a particular technology or combination of technologies, without establishing any a priori design. By finding performance limits on chemical process networks, IDEAS allows the detection of process intensification candidates, the comparison between different intensified approaches, and quantifies the potential for further improvements.

The IDEAS conceptual framework has been successfully applied to either globally optimize, or to identify the attainable region for, various types of process networks. Some IDEAS applications include the synthesis of multicomponent mass exchange networks (Wilson and Manousiouthakis, 2000), ideal distillation networks (Drake and Manousiouthakis, 2002a,b), separator networks (Justanieah and Manousiouthakis, 2003), power cycles (Martin and Manousiouthakis, 2003), heat/power integrated distillation networks (Holiastos and

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Notation

Thermodynamic Variables

P	Reactive flash separator pressure (Pa)
T	Reactive flash separator temperature (K)
$y_k^V(i)$	k^{th} species equilibrium vapor composition leaving the i^{th}unit (dim)
$x_k^L(i)$	k^{th} species equilibrium liquid composition leaving the i^{th}unit (dim)
$P_k^{sat}(T)$	k^{th} species temperature dependent saturated vapor pressure (Pa)
$\phi_k\left(\left\{y_l^V\right\}_{l=1}^n, T, P\right)$	k^{th}Species non-ideal fugacity coefficient
$\gamma_k\left(\left\{x_l^L\right\}_{l=1}^n, T\right)$	k^{th}Species non-ideal liquid activity coefficient
a_k	Activity of the k^{th}species (dim)
$A_{j,k}$	Antoine equationj^{th} parameter of the k^{th}species (dim)
K_{eq}	Reaction equilibrium constant (dim)
k_f	Forward reaction rate constant (1/h)

IDEAS Variables:

$F^I(i)$	i^{th}DN inlet stream
$F^O(i)$	i^{th}DN outlet stream
$F^L(i)$	i^{th} OP liquid outlet
$F^V(i)$	i^{th} OP vapor outlet
$F^{OI}(i,j)$	j^{th}DN inlet stream to i^{th}DN outlet
$F^{PI}(i,j)$	i^{th} OP inlet stream from j^{th}DN network inlet
$F^{OL}(i,j)$	i^{th} DN outlet stream from j^{th}OP liquid outlet
$F^{OV}(i,j)$	i^{th} DN outlet stream from j^{th}OP vapor outlet
$F^{PL}(i,j)$	i^{th} OP inlet stream from j^{th}OP liquid outlet
$F^{PV}(i,j)$	i^{th} OP inlet stream from j^{th}OP vapor outlet
$H(i)$	Reactive holdup of the i^{th} reactive flash separator unit in the OP
$C(i)$	Capacity of the i^{th} reactive flash separator unit in the OP
$z_k^I(i)$	k^{th}species, i^{th}DN inlet stream composition
$z_k^O(i)$	k^{th}species, i^{th}DN outlet stream composition
$\left(z_k^O(i)\right)^l$	k^{th}species, i^{th}DN outlet stream composition vector, lower bound
$\left(z_k^O(i)\right)^u$	k^{th}species, i^{th}DN outlet stream composition vector, upper bound
$x_k^L(i)$	k^{th}species, i^{th}OP liquid outlet composition
$y_k^V(i)$	k^{th}species, i^{th}OP vapor outlet composition
G	Total number of reactive flashes in the OP
M	Number of IDEAS network inlets
N	Number of IDEAS network outlets

Manousiouthakis, 2004), reactive distillation networks (Burri and Manousiouthakis, 2004), reactor network attainable region (Burri et al., 2002; Manousiouthakis et al., 2004; Zhou and Manousiouthakis, 2006; Zhou and Manousiouthakis, 2007a,b; Posada and Manousiouthakis, 2008; Zhou and Manousiouthakis, 2008a; Zhou and Manousiouthakis, 2009; Ghougassian and Manousiouthakis, 2013), azeotropic distillation networks (Ghougassian and Manousiouthakis, 2012), reactor networks (Zhou and Manousiouthakis, 2008b; Al-Husseini and Manousiouthakis, 2014; Ghougassian and Manousiouthakis, 2015), batch reactor networks (Davis et al., 2008), and process network attainable region (Conner and Manousiouthakis 2014).

Derived by using simple physical concepts, IDEAS can be potentially applied to design and globally optimize virtually any chemical process. One of the key concepts behind the IDEAS framework can be visualized by considering, as a process operation example, a steady-state CSTR model as shown in Fig. 1a and represented by Eq. (1). Usually, the design objective is to find an optimal H (variable) that can deliver a specified output C_i^{OUT} from a known input C_i^{IN}. This formulation is clearly nonlinear since the reaction rate $R_i(T)$ is also a variable.

$$\begin{aligned} &FC_i^{IN} - FC_i^{OUT} + R_i(T)H = 0 \quad ; \\ &\quad i = 1, n \quad ; \quad T \in D = \left\{T \in \mathbb{R} \mid T^{lb} \le T \le T^{ub}\right\} \end{aligned} \tag{1}$$

In the IDEAS approach, a part of the process output is considered to vary linearly with a part of the process input, when certain variables are considered constant. In the CSTR example, by converting the temperature domain D into a bounded series containing infinite elements, as shown in Eq. (2), it is possible to calculate a unique reaction rate R_i^k for each CSTR according to the elements of the series.

$$\begin{aligned} &FC_i^{IN} - FC_i^{OUT} + R_i^k(T)H = 0 \quad ; \\ &\quad T \in D = \left\{T^k\right\}_{k=1}^{\infty} \wedge \left\{T \mid T^{lb} \le T \le T^{ub}\right\} \end{aligned} \tag{2}$$

As a result, IDEAS introduces several standalone units with different characteristics, covering the domain of the respective linearized variable as shown in Fig. 1b. The set of standalone units in IDEAS framework is called process operator (OP). From the process synthesis

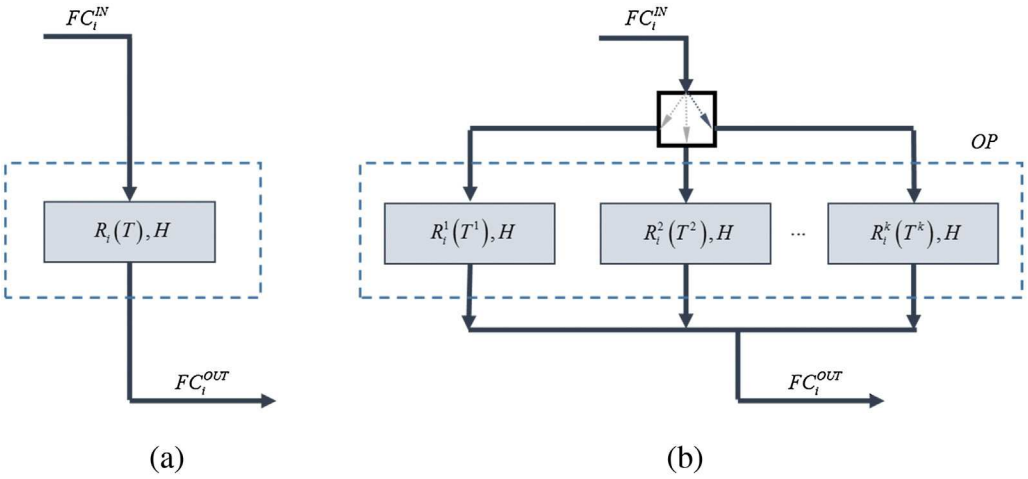

Fig. 1. Example of a steady-state CSTR design model: (a) Nonlinear traditional approach, (b) IDEAS linear process operator approach.

point of view, considering that the OP set has an infinite number of standalone linear units and each unit can be individually activated by a distribution system, then any possible configuration taken by the standalone nonlinear unit in a synthesis procedure is contained in the IDEAS-OP. Despite the fact that IDEAS contemplates any design configuration obtained from a nonlinear unit, it is easy to verify that the infinite OP maintains its linearity feature for any chemical process.

In the IDEAS framework, all units in the OP can be used to reach the desired process objective. A flow operator structure, the IDEAS distribution network DN, is employed to connect all inlet-outlet possibilities (i.e., process inlets to process units, process inlets to process outlets, process units to process units and process units to process outlets). Considering that the DN operations (mixing, splitting, recycling, and bypass) are linear in the flow variables, the IDEAS DN-OP representation is linear for any chemical process. The structure of IDEAS guarantees that all possible process flowsheets are taken into account in the network synthesis problem for an a priori given set of phenomena.

Due to IDEAS' innovative proposition for the process operations, which domain and range is considered to lie in an infinite (rather than finite) dimensional space, infinite dimensional linear programs (ILP) can be formulated for the synthesis of optimal process networks. In fact, since it is not possible to solve an ILP, its solution is approximated arbitrarily close by finite dimensional linear programs (LP) of ever increasing size. The sequence formed by the LP optimal solutions converges to the global optimal solution of the ILP.

Even though the application of the IDEAS framework can lead to large LPs, in practice, IDEAS can generate very impressive results with relatively small LPs. Additionally, IDEAS features increase the possibility of finding a breakthrough in process synthesis. In this paper, the IDEAS framework is applied as a systematic design tool for reactive separation process intensification seeking minimum reactive holdup and minimum total capacity.

2. Mathematical formulation

2.1. Reactive flash separator model

The focus of this work is the synthesis of networks of reactive flash separators. In the work developed by Burri and Manousiouthakis (2004), reactive flash separators were employed for the systematic synthesis of reactive distillation networks. Other models have also been proposed to design and optimize reactive distillation systems. Procedures based on geometrical approaches, such as the residue curve maps and the fixed point method have been heavily utilized to attack the problem (Barbosa and Doherty, 1988; Venimadhavan et al., 1994; Siirola, 1996; Okasinski and Doherty, 1998; Malone and Doherty, 2000; Chen et al., 2000; Barnicki et al., 2000; Jiménez et al., 2001; Huss et al., 2003; Li et al., 2016). In addition to the graphical approach, optimization-based methods using mixed-integer nonlinear programming (MINPL) formulations (Ciric and Gu, 1994; Papalexandri and Pistikopoulos, 1996; Jackson and Grossmann, 2001; Georgiadis et al., 2002; Cardoso et al., 2000; Hoffmaster and Hauan, 2006; Avami et al., 2012; Urselmann and Engell, 2015) or infinite linear programming (ILP) formulations (Burri and Manousiouthakis, 2004) have also contributed to the advancement of reactive distillation process synthesis.

Focusing on process intensification concepts, in this work we present a series of improvements in the general approach presented by Burri and Manousiouthakis (2004) for the systematic synthesis of reactive distillation networks. In this improved model, an isothermal, isobaric, reactive flash separator is considered, as shown in Fig. 2. The reactive flash separator's vapor and liquid exit streams are considered to be in phase equilibrium with one another, and reactions may occur in the liquid phase, depending on the reactive volume H (the reactive holdup) of the flash separator. In addition, a capacity variable C, associated with the total liquid holdup, is also considered.

This approach gives to the reactive flash the ability to account for several phenomena that can act together or in isolation, depending on the needs of the synthesis process. A fully operational reactive flash will simultaneously act as both a reactor and VLE separator. Moreover, if the reactive holdup is zero, the process acts only as a VLE flash separator; and if no separation takes place, the process assumes the behavior

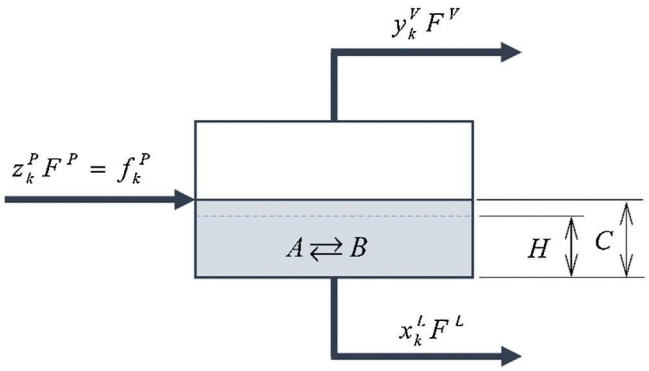

Fig. 2. Representation of the reactive flash separator.

of an isolated CSTR reactor, with only one liquid flow as output. The component balance formulation for the reactive flash separator model is shown in Eq. (3):

$$f_k^P + R_k\left(\left\{x_j^L\right\}_{j=1}^n, T, P\right) H - x_k^L F^L - y_k^V F^V = 0 \quad ; \quad \forall k = 1, \ldots, n \tag{3}$$

The general formulation for the phase equilibrium condition of each k^{th}-component in the mixture uses the Gamma-Phi model to relate the liquid molar fraction x_k^L with the correspondent vapor molar fraction y_k^V inside the reactive flash separator, as shown in Eq. (4):

$$y_k^V \phi_k\left(\left\{y_l^V\right\}_{l=1}^n, T, P\right) P = x_k^L \gamma_k\left(\left\{x_l^L\right\}_{l=1}^n, T\right) P_k^{sat}(T); \quad \forall k = 1, \ldots, n \tag{4}$$

The k^{th}-component's generation rate R_k in the reactive flash is usually given by a kinetic rate expression in the form of Eq. (5), although other rate forms are also possible.

$$R_k = k_f(T)\left(\prod_{reactants} a_r(\gamma_r, x_r)^{\nu_r} - \frac{1}{K_{eq}(T)} \prod_{products} a_p\left(\gamma_p, x_p\right)^{\nu_p}\right) \tag{5}$$

The species i activity in a multicomponent mixture is related to the activity coefficient in the liquid phase and the liquid molar fraction for the respective component as shown in Eq. (6).

$$a_i = \gamma_i\left(\left\{x_l^L\right\}_{l=1}^n, T\right) x_i \tag{6}$$

In order to solve the vapor-liquid equilibrium model showed in Eq. (4), a variety of thermodynamic models can be utilized to describe the behavior of the fugacity coefficient function $\phi_k\left(\left\{y_l^V\right\}_{l=1}^n, T, P\right)$, the activity coefficient function $\gamma_k\left(\left\{x_l^L\right\}_{l=1}^n, T\right)$ and the saturated pressure $P_k^{sat}(T)$ for the k^{th}-component in the mixture. Since vapor-liquid equilibrium is assumed in the reactive flash and considering ideal gas behavior, for each specified composition in the liquid output the specified thermodynamic models can be iteratively calculated for different temperatures until the vapor fractions sum up to unity. This procedure was successfully applied by Burri and Manousiouthakis (2004) and by Ghougassian and Manousiouthakis (2012), in which the Wilson and the Antoine equation were used to express the components' non-ideal liquid activity coefficients and partial pressures respectively. Since the selection of these models depends on the information available, which can vary from each case, the models used will be presented in the application example (Section 3.1).

In the IDEAS ILP formulation, an infinite number of the aforementioned reactive flash separators are presented in the process operator (OP). The ILP formulation is presented in the next section.

2.2. IDEAS ILP for the reactive flash separator synthesis problem

In order to consider all possible flowsheets for the reactive flash separator network, the process operator OP is interfaced with a distribution network (DN) where all stream splitting, mixing and pressure adjustment occurs. Fig. 3 shows the resulting IDEAS framework for the reactive flash separator synthesis problem.

Each of the cross-flow streams in the DN is characterized by a flow rate variable, which has fixed origin molar fraction conditions. The flow variables are identified by a superscript that indicates their destination and source respectively: the DN inlet is identified as I, the DN outlet as O, the OP inlet as P, the liquid and vapor outputs from the OP as L and V respectively. The flow variables also feature indices designating the destination-source pair structure. The reactive holdups and the capacity are both variables associated with the elements of the OP.

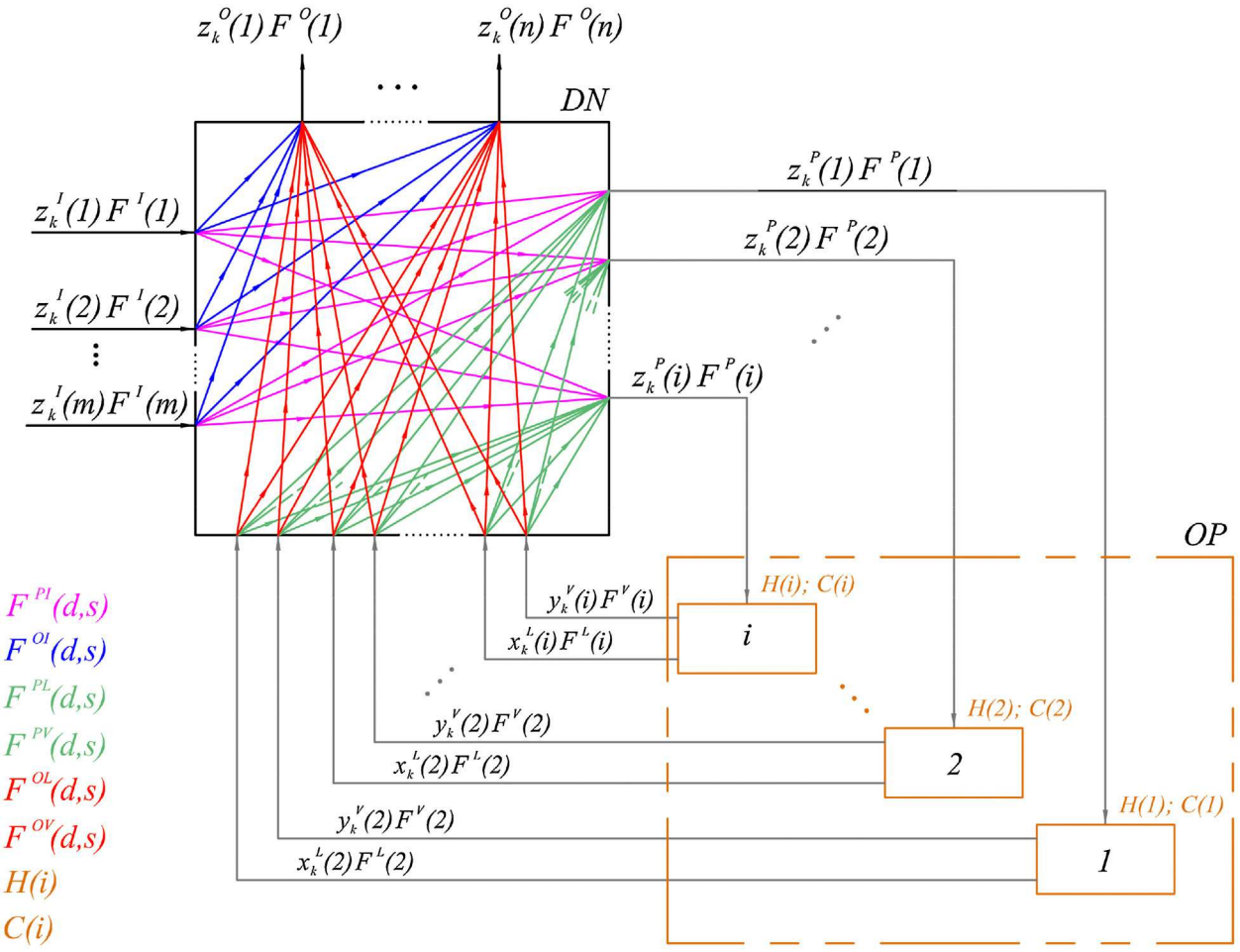

Fig. 3. IDEAS representation for a reactive flash separator network.

Several infinite LP formulations can be derived using the IDEAS framework. In order to simplify the application on the case study, a general ILP formulation is developed that can be modified for any specific case. A generic linear objective function is proposed at this point, as

$$c^T F \tag{7}$$

where the vector F includes all flows of the DN, the inlet flows, the reactive holdups for the reactive flashes and their respective capacity. The above objective function can be used to realize a wide array of objectives, through appropriate selection of the elements of the cost vector c^T.

The development of the constraints for the ILP general formulation uses mass and component balances on the DN, and the proposed reactive flash separator model for the OP. For each inlet flow $F^I(j)$ associated with one of the M inlets of the DN, a splitting balance is written as shown in Eq. (8).

$$F^I(j) - \sum_{i=1}^{N} F^{OI}(i,j) - \sum_{i=1}^{\infty} F^{PI}(i,j) = 0 \quad ; \quad \forall j = 1, \ldots, M \tag{8}$$

For each outlet flow $F^O(i)$ leaving the DN from one of its N outlets, a mixing balance as shown in Eq. (9) is considered.

$$F^O(i) - \sum_{j=1}^{M} F^{OI}(i,j) - \sum_{j=1}^{\infty} F^{OL}(i,j) - \sum_{j=1}^{\infty} F^{OV}(i,j) = 0 \quad ; \quad \forall i = 1, \ldots, N \tag{9}$$

The component flow $f_k^P(i)$ that feeds the i^{th} reactive flash separator can be considered as the sum of component flows feeding that specific mixing point of the DN (component balance).

$$f_k^P(i) - \sum_{j=1}^{M} z_k^I(j) F^{PI}(i,j) - \sum_{j=1}^{\infty} x_k^L(j) F^{PL}(i,j) - \sum_{j=1}^{\infty} y_k^V(j) F^{PV}(i,j) = 0 \quad ; \quad \begin{matrix} \forall i = 1, \ldots, \infty \\ \forall k = 1, \ldots, n \end{matrix} \tag{10}$$

Thus, the total mass flow in this mixing node is represented by Eq. (11) below.

$$F^P(i) - \sum_{j=1}^{M} F^{PI}(i,j) - \sum_{j=1}^{\infty} F^{PL}(i,j) - \sum_{j=1}^{\infty} F^{PV}(i,j) = 0 \; ; \qquad \forall i = 1, \ldots, \infty \tag{11}$$

For each $F^L(j)$ liquid and $F^V(j)$ vapor input flow entering the DN's after being processed in the OP, a splitting balance is written as:

$$F^L(j) - \sum_{i=1}^{N} F^{OL}(i,j) - \sum_{i=1}^{\infty} F^{PL}(i,j) = 0 \; ; \quad \forall j = 1, \ldots, \infty \tag{12}$$

$$F^V(j) - \sum_{i=1}^{N} F^{OV}(i,j) - \sum_{i=1}^{\infty} F^{PV}(i,j) = 0 \; ; \quad \forall j = 1, \ldots, \infty \tag{13}$$

The final products from the reactive distillation process can be found in the DN outlets. Lower and upper bound constraints are introduced on each of the N flow variables $F^O(i)$ as design parameters. The total balance for each flow exiting the DN is shown in Eq. (14).

$$\left(F^O(i)\right)^l \le \sum_{j=1}^{M} F^{OI}(i,j) + \sum_{j=1}^{\infty} F^{OL}(i,j) + \sum_{j=1}^{\infty} F^{OV}(i,j) \le \left(F^O(i)\right)^u \; ; \qquad \forall i = 1, \ldots, N \tag{14}$$

Eq. (14) can also be expressed by two independent inequalities as shown below:

$$\left[\sum_{j=1}^{M} F^{OI}(i,j) + \sum_{j=1}^{\infty} F^{OL}(i,j) + \sum_{j=1}^{\infty} F^{OV}(i,j)\right] - \left(F^O(i)\right)^l \ge 0 \quad ; \quad \forall i = 1, \ldots, N \tag{15}$$

$$\left[\sum_{j=1}^{M} F^{OI}(i,j) + \sum_{j=1}^{\infty} F^{OL}(i,j) + \sum_{j=1}^{\infty} F^{OV}(i,j)\right] - \left(F^O(i)\right)^u \le 0 \quad ; \quad \forall i = 1, \ldots, N \tag{16}$$

The component balances at the DN's outputs, including upper and lower bounds for the product's molar fractions are represented by Eq. (17).

$$\left(z_k^O(i)\right)^l F^O(i) \le \left\{ \begin{array}{l} \sum_{j=1}^{M} z_k^I(j) F^{OI}(i,j) \\ + \sum_{j=1}^{\infty} x_k^L(j) F^{OL}(i,j) \\ + \sum_{j=1}^{\infty} y_k^V(j) F^{OV}(i,j) \end{array} \right\} \le \left(z_k^O(i)\right)^u F^O(i) \quad ; \quad \begin{matrix} \forall i = 1, \ldots, N \\ \forall k = 1, \ldots, n \end{matrix} \tag{17}$$

Finally, the balances for the reactive flash separators in the OP are expressed as shown in Eq. (18).

$$f_k^P(i) + R_k(i) H(i) - x_k^L(i) F^L(i) - y_k^V(i) F^V(i) = 0 \quad ; \quad \begin{matrix} \forall i = 1, \ldots, \infty \\ \forall k = 1, \ldots, n \end{matrix} \tag{18}$$

A minimum residence time τ is proposed for the feasible reactive flash separators in the network. The capacity of each reactive flash in the OP is determined by either the reactive holdup, Eq. (19), or the residence time times the reactive flash inlet flow, Eq. (20), whichever is greater.

$$C(i) \ge H(i) \quad ; \quad \forall i = 1, \ldots, \infty \tag{19}$$

$$C(i) \ge \tau F^P(i) \quad ; \quad \forall i = 1, \ldots, \infty \tag{20}$$

By substituting Eq. (11) in Eq. (20), the capacity must then satisfy:

$$C(i) \ge \tau \left[\sum_{j=1}^{M} F^{PI}(i,j) + \sum_{j=1}^{\infty} F^{PL}(i,j) + \sum_{j=1}^{\infty} F^{PV}(i,j)\right] \quad ; \quad \forall i = 1, \ldots, \infty \tag{21}$$

The number of variables can be reduced by substituting Eq. (8)–(10) in Eq. (18):

$$R_k(i)H(i) - x_k^L(i)\left[\sum_{j=1}^{N} F^{OL}(j,i) + \sum_{j=1}^{\infty} F^{PL}(j,i)\right] - y_k^V(i)\left[\sum_{j=1}^{N} F^{OV}(j,i) + \sum_{j=1}^{\infty} F^{PV}(j,i)\right] + \sum_{j=1}^{M} z_k^I(j)F^{PI}(i,j)$$
$$+\sum_{j=1}^{\infty} x_k^L(j)F^{PL}(i,j) + \sum_{j=1}^{\infty} y_k^V(j)F^{PV}(i,j) = 0 \quad ; \quad \begin{matrix}\forall i = 1,\ldots,\infty \\ \forall k = 1,\ldots,n\end{matrix} \tag{22}$$

From Eq. (22), self-recycling flows are naturally eliminated from the system. This fact can lead to further simplifications as shown in Eq. (23):

$$R_k(i)H(i) + \sum_{j=1}^{M} z_k^I(j)F^{PI}(i,j) - \sum_{j=1}^{N} x_k^L(i)F^{OL}(j,i) - \sum_{j=1}^{N} y_k^V(i)F^{OV}(j,i) + \sum_{\substack{j=1 \\ j\neq i}}^{\infty}\left[x_k^L(j)F^{PL}(i,j) - x_k^L(i)F^{PL}(j,i)\right]$$
$$+\sum_{\substack{j=1 \\ j\neq i}}^{\infty}\left[y_k^V(j)F^{PV}(i,j) - y_k^V(i)F^{PV}(j,i)\right] = 0 \; ; \; \begin{matrix}\forall i = 1,\ldots,\infty \\ \forall k = 1,\ldots,n\end{matrix} \tag{23}$$

Some variables in the component outlet bounds equations can be eliminated substituting Eq. (9) in Eq. (17):

$$\left(z_k^O(i)\right)^l \left[\begin{matrix}\sum_{j=1}^{M} F^{OI}(i,j) \\ +\sum_{j=1}^{\infty} F^{OL}(i,j) \\ +\sum_{j=1}^{\infty} F^{OV}(i,j)\end{matrix}\right] \leq \left[\begin{matrix}\sum_{j=1}^{M} z_k^I(j)F^{OI}(i,j) \\ +\sum_{j=1}^{\infty} x_k^L(j)F^{OL}(i,j) \\ +\sum_{j=1}^{\infty} y_k^V(j)F^{OV}(i,j)\end{matrix}\right] \leq \left(z_k^O(i)\right)^u \left[\begin{matrix}\sum_{j=1}^{M} F^{OI}(i,j) \\ +\sum_{j=1}^{\infty} F^{OL}(i,j) \\ +\sum_{j=1}^{\infty} F^{OV}(i,j)\end{matrix}\right] \; ; \; \begin{matrix}\forall i = 1,\ldots,N \\ \forall k = 1,\ldots,n\end{matrix} \tag{24}$$

Moreover, Eq. (24) can then be split into two inequalities:

$$\sum_{j=1}^{M}\left[\left(\left(z_k^O(i)\right)^l - z_k^I(j)\right)F^{OI}(i,j)\right] + \sum_{j=1}^{\infty}\left[\left(\left(z_k^O(i)\right)^l - x_k^L(j)\right)F^{OL}(i,j)\right] + \sum_{j=1}^{\infty}\left[\left(\left(z_k^O(i)\right)^l - y_k^V(j)\right)F^{OV}(i,j)\right] \leq 0 \; ; \; \begin{matrix}\forall i = 1,\ldots,N \\ \forall k = 1,\ldots,n\end{matrix} \tag{25}$$

$$\sum_{j=1}^{M}\left[\left(\left(z_k^O(i)\right)^u - z_k^I(j)\right)F^{OI}(i,j)\right] + \sum_{j=1}^{\infty}\left[\left(\left(z_k^O(i)\right)^u - x_k^L(j)\right)F^{OL}(i,j)\right] + \sum_{j=1}^{\infty}\left[\left(\left(z_k^O(i)\right)^u - y_k^V(j)\right)F^{OV}(i,j)\right] \geq 0 \; ; \; \begin{matrix}\forall i = 1,\ldots,N \\ \forall k = 1,\ldots,n\end{matrix} \tag{26}$$

In order to make it easier to calculate and restrict the total size of the network, a total capacity constraint with upper bound C^{ub} was modeled. This constraint is used in the intensification procedure to enable the search for the smallest feasible network size for the specified problem and is presented in Eq. (27).

$$\sum_{i=1}^{\infty} C(i) \leq C^{ub} \tag{27}$$

The final general ILP formulation for the reactive distillation network synthesis has a general objective function as shown in Eq. (7) subject to the constraints represented by Eqs. (8), (15), (16), (19), (21), (23), (25), (26) and (27), summarized below:

$$\nu \triangleq \inf \; c^T F$$

$$s.t.$$

$$F^I(j) - \sum_{i=1}^{N} F^{OI}(i,j) - \sum_{i=1}^{\infty} F^{PI}(i,j) = 0 \qquad \forall j = 1,\ldots,M$$

$$\left[\sum_{j=1}^{M} F^{OI}(i,j) + \sum_{j=1}^{\infty} F^{OL}(i,j) + \sum_{j=1}^{\infty} F^{OV}(i,j)\right] - \left(F^O(i)\right)^l \geq 0 \qquad \forall i = 1,\ldots,N$$

$$\left[\sum_{j=1}^{M} F^{OI}(i,j) + \sum_{j=1}^{\infty} F^{OL}(i,j) + \sum_{j=1}^{\infty} F^{OV}(i,j)\right] - \left(F^{O}(i)\right)^{u} \leq 0 \qquad \forall i = 1, \ldots, N$$

$$C(i) \geq H(i) \qquad \forall i = 1, \ldots, \infty$$

$$C(i) \geq \tau \left[\sum_{j=1}^{M} F^{PI}(i,j) + \sum_{j=1}^{\infty} F^{PL}(i,j) + \sum_{j=1}^{\infty} F^{PV}(i,j)\right] \qquad \forall i = 1, \ldots, \infty$$

$$R_k(i)H(i) + \sum_{j=1}^{M} z_k^{I}(j) F^{PI}(i,j) - \sum_{j=1}^{N} x_k^{L}(i) F^{OL}(j,i) - \sum_{j=1}^{N} y_k^{V}(i) F^{OV}(j,i)$$
$$+ \sum_{\substack{j=1 \\ j \neq i}}^{\infty} \left[x_k^{L}(j) F^{PL}(i,j) - x_k^{L}(i) F^{PL}(j,i)\right] + \sum_{\substack{j=1 \\ j \neq i}}^{\infty} \left[y_k^{V}(j) F^{PV}(i,j) - y_k^{V}(i) F^{PV}(j,i)\right] = 0 \qquad \begin{matrix} \forall i = 1, \ldots, \infty \\ \forall k = 1, \ldots, n \end{matrix}$$

$$\sum_{j=1}^{M} \left[\left(\left(z_k^{O}(i)\right)^{l} - z_k^{I}(j)\right) F^{OI}(i,j)\right] + \sum_{j=1}^{\infty} \left[\left(\left(z_k^{O}(i)\right)^{l} - x_k^{L}(j)\right) F^{OL}(i,j)\right]$$
$$+ \sum_{j=1}^{\infty} \left[\left(\left(z_k^{O}(i)\right)^{l} - y_k^{V}(j)\right) F^{OV}(i,j)\right] \leq 0 \qquad \begin{matrix} \forall i = 1, \ldots, N \\ \forall k = 1, \ldots, n \end{matrix}$$

$$\sum_{j=1}^{M} \left[\left(\left(z_k^{O}(i)\right)^{u} - z_k^{I}(j)\right) F^{OI}(i,j)\right] + \sum_{j=1}^{\infty} \left[\left(\left(z_k^{O}(i)\right)^{u} - x_k^{L}(j)\right) F^{OL}(i,j)\right]$$
$$+ \sum_{j=1}^{\infty} \left[\left(\left(z_k^{O}(i)\right)^{u} - y_k^{V}(j)\right) F^{OV}(i,j)\right] \geq 0 \qquad \begin{matrix} \forall i = 1, \ldots, N \\ \forall k = 1, \ldots, n \end{matrix}$$

$$\sum_{i=1}^{\infty} C(i) \leq C^{ub}$$

$$F^{I} \geq 0\ ;\ F^{O} \geq 0\ ;\ F^{OI} \geq 0\ ;\ F^{PI} \geq 0\ ;\ F^{OL} \geq 0\ ;\ F^{OV} \geq 0\ ;\ F^{PL} \geq 0\ ;\ F^{PV} \geq 0\ ;\ H \geq 0\ ;\ C \geq 0$$

2.3. ILP approximation by finite LPs

An infinite dimensional linear program cannot be explicitly solved. However, its solution can be approximated by a series of finite linear programs of increasing size, whose sequence of optimum values converges to the infinite dimensional problem's infimum. In particular, instead of an infinite number, consider a finite set containing G reactive flash separators in the OP. Consequently, the aforementioned IDEAS infinite LP formulation becomes a finite LP, which is a convex problem and can be solved by any LP solver.

Considering that the finite LP can now be solved η times using an ever increasing number G of reactive flash separators, i.e. $G(1) < G(2) < \ldots < G(\eta)$, the resulting optimal values of these finite linear programs form a non-increasing sequence $\nu(1) > \nu(2) > \ldots > \nu(\eta)$, which converges to the infimum of the ILP when $\eta \to \infty$. This evolution of the optimal solution is shown in the case study.

3. Case study: Olefin metathesis

3.1. Thermodynamic data and problem specifications

In this section, the proposed IDEAS framework formulation is applied to the design of an intensified reactive distillation network for the metathesis of 2-pentene to form 2-butene and 3-hexene as shown in Eq. (28).

$$2C_5H_{10} \rightleftarrows C_4H_8 + C_6H_{12} \tag{28}$$

Metathesis reactions are important for rebalancing the light olefins in both catalytic and steam cracking. The interest in applying reactive distillation systems on the metathesis of 2-pentene is reflected in the literature (Al-Arfaj and Luyben, 2002; Chadda et al., 2000; Chen et al., 2000; Hoffmaster and Hauan, 2006; Jackson and Grossmann, 2001; Li et al., 2012; Okasinski and Doherty, 1998).

Table 1
Antoine coefficients for 2-butene, 2-pentene, 3-hexene (Okasinski and Doherty 1998).

	$k = C_4H_8$	$k = C_5H_{10}$	$k = C_6H_{12}$
$A_{1,k}$	20.73426	20.89774	21.0311
$A_{2,k}$	−2755.642	−3090.783	−3366.99
$A_{3,k}$	−53.989	−53.963	−58.04

Considering 2-pentene as the reference component, the temperature dependent rate expression is given by Eq. (29) (Chen et al., 2000):

$$R = k_f \left(a_{C_5H_{10}}^2 - \frac{a_{C_4H_8}\ a_{C_6H_{12}}}{K_{eq}} \right) \tag{29}$$

The reaction equilibrium constant K_{eq} and the kinetic rate constant $k_f\ \left(h^{-1}\right)$ are shown in Eqs. (30) and (31) respectively.

$$K_{eq} = 0.25 \tag{30}$$

$$k_f = 1.0661\ \times\ 10^5\ e^{\left(-3321.2/T(K)\right)}\ \left(h^{-1}\right) \tag{31}$$

This system is a candidate for reactive distillation because butane is the low boiling component, whose removal from the liquid reacting mixture as vapor favors conversion since it is readily separated away from the reactive zone. This reaction occurs at atmospheric pressure and has negligible heat of reaction. Moreover, since this system shows ideal vapor-liquid equilibrium, both the fugacity $\phi_k\left(\left\{y_l^V\right\}_{l=1}^n, T, P\right)$ and the activity $\gamma_k\left(\left\{x_l^L\right\}_{l=1}^n, T\right)$ coefficient functions showed in Eq. (4) are equal the unity and Raoult's law is assumed. In addition, the species' activities in Eq. (29) take the values of the respective molar fractions. The saturated pressure of the mixture is calculated by using Antoine's equation, the coefficients of which can be found in Table 1 for T in K and P in Pa. Thus, for a fixed operational pressure P and for the specified liquid outlet composition of each i reactive flash separator, the respective bubble point temperature, reaction rate, and vapor outlet composition is iteratively changing $T(i)$ in Eq. (32) until the condition specified in Eq. (35) is reached.

$$\ln P_k^{sat}(i) = A_{1,k} + \frac{A_{2,k}}{T(i) + A_{3,k}};\ \forall k = C_5H_{10}, C_8H_8, C_6H_{12} \tag{32}$$

$$y_k^V(i) = \frac{x_k^L(i) P_k^{sat}(T(i))}{P};\ \forall k = C_5H_{10}, C_8H_8, C_6H_{12} \tag{33}$$

$$R(i) = 1.0661\ \times\ 10^5\ e^{\left(-3321.2/T(i)\right)} \left[\left(x_{C_5H_{10}}(i)\right)^2 - \frac{x_{C_4H_8}(i)\ x_{C_6H_{12}}(i)}{0.25} \right] \tag{34}$$

$$y_{C_5H_{10}}^V(i) + y_{C_4H_8}^V(i) + y_{C_6H_{12}}^V(i) - 1 = 0 \tag{35}$$

In order to perform the reactive distillation process, the distribution network of IDEAS is set to have one inlet stream, containing pure pentene, and two outlets streams according to the specifications for the final products as shown in Table 2.

3.2. Objective function

This work focuses on reactive separation systems, quantifying rigorous tradeoffs between the network's total reactive holdup and its total capacity. In doing so it can assess what is the potential for process intensification compared to designs proposed in the literature. The tradeoff is quantified rigorously by repeatedly minimizing the reactive holdup (objective function) while constraining the system's total capacity to be lower than an ever decreasing sequence of upper bounds C^{ub}, Eq. (27). The total reactive holdup is a surrogate for capital costs

Table 2
Specifications for the 2-pentene metathesis problem example.

Feed Flow (kmol/h)	100
Outlet Flow 1 (Distillate) (kmol/h)	50
Outlet Flow 2 (Bottom) (kmol/h)	50
Residence Time (s)	60
Operating pressure (bar)	1
Inlet molar fractions	
C4H8	0.0000
C5H10	1.0000
C6H12	0.0000
Outlet molar fraction target bounds	
Outlet Flow 1	
C4H8	0.9800–1.0000
C5H10	0.0000–0.2000
C6H12	0.0000–0.2000
Outlet Flow 2	
C4H8	0.0000–0.2000
C5H10	0.0000–0.2000
C6H12	0.9800–1.0000

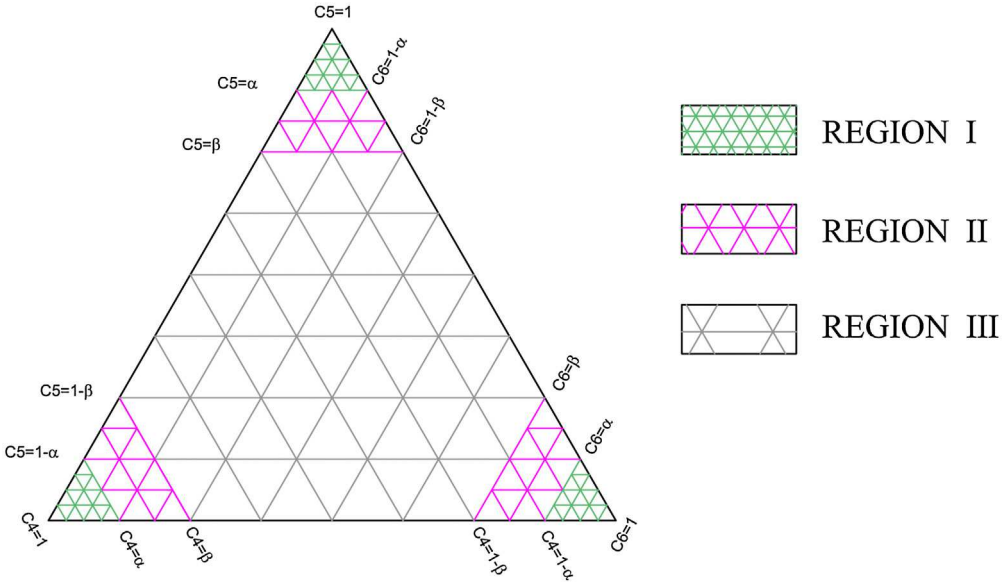

Fig. 4. Discretization of ternary mixture's liquid molar fraction domain.

associated with reactors, in particular the amount of catalyst used to carry out the reaction (Biegler et al., 1997, p. 118; Towler and Sinnott, 2012, p. 324). The system's total capacity is a surrogate for capital costs associated with vessels (e.g. flashes), and is also a surrogate for operating costs, as it is proportional to the network's total flowrate, which in turn is a surrogate for the reactive separation system's energy consumption, as higher energy consumption results in higher material flows within the network, (Biegler et al., 1997, p. 122; Towler and Sinnott, 2012, p. 324).

The resulting IDEAS' finite LP formulation is shown in Eq. (36).

$$\begin{aligned} &\min \sum_{i=1}^{G} H(i) \\ &\text{s.t.} \\ &\text{Eqs.(8), (15), (16), (19), (21), (23), (25), (26) and(27)} \\ &\text{All variables} \geq 0 \end{aligned} \tag{36}$$

The LP problem in Eq. (36) is solved several times with an increasingly smaller value for the capacity upper bound until it reaches the feasibility limit, which allows the identification of the minimum capacity needed to deliver the desired purity specifications for the reactive distillation network.

3.3. Discretization strategy and IDEAS convergence

To generate the set of reactive flash separators, establishing the IDEAS OP for the finite LP problem, the ternary mixture's liquid composition (molar fraction) domain is discretized.

The impact of a non-uniform discretization in the generation of the IDEAS OP is investigated in this work. For a three-component system, such as the metathesis of 2-pentene, the liquid's molar fraction domain is represented by a traditional triangular diagram, where each vertex represents a pure substance and the sum of the species molar fractions is equal to unity, for any point inside the triangle. The ternary mixture's liquid molar fraction domain was divided into three regions as shown in Fig. 4. Different discretization steps are allowed in each of the proposed regions, whose edges are specified by the molar fractions α and β.

This procedure allows the generation of more reactive flash separators in regions where the separation is more difficult, such as close to the high purity points, controlling the growth of the cardinality G of the universe of considered reactive flash separators. The minimization of the total reactive holdup H was performed for a variety of discretization steps, as shown in Table 3. Results were obtained for $\alpha = 0.875$ and $\beta = 0.75$as the region edges, and minimum purity of 87.5% for both butane and hexene.

This assessment reveals that, for this minimization problem, the optimal value depends strongly on the discretization of region I, which is related to the set of reactive flash separators used to obtain each of the components in the mixture at high purity. Beyond some discretization level, the size of the discretized steps in regions II and III did not change the optimal value of the total reactive holdup.

As indicated in Section 2.3, the infimum of the IDEAS ILP is approximated through a convergent series composed by the solutions of the finite LP for an ever smaller discretized step size, i.e., an ever increasing number of reactive separator flash units G. For the conditions specified in this assessment, a convergence plot of IDEAS framework for the discretized set in Table 4 is shown in Fig. 5.

Table 3
Optimal total reactive holdup (87.5% purity) per discretized set in regions I, II and III.

Discretized step size			Optimum total reactive holdup
Region I	Region II	Region III	
1/8	1/8	1/8	Infeasible
1/16	1/8	1/8	Infeasible
1/32	1/8	1/8	Infeasible
1/64	1/8	1/8	596.74
1/128	1/8	1/8	378.66
1/16	1/16	1/8	416.99
1/32	1/16	1/8	394.15
1/64	1/16	1/8	381.46
1/128	1/16	1/8	376.79
1/16	1/16	1/16	65.44
1/32	1/16	1/16	61.6
1/64	1/16	1/16	42.24
1/128	1/16	1/16	39.64
1/32	1/32	1/16	48.31
1/64	1/32	1/16	42.24
1/128	1/32	1/16	39.64
1/32	1/32	1/32	48.31
1/64	1/32	1/32	42.24
1/128	1/32	1/32	39.64
1/64	1/64	1/16	42.24
1/128	1/64	1/16	39.64
1/64	1/64	1/32	42.24
1/128	1/64	1/32	39.64

Table 4
Discretized set in regions I, II and III utilized in the IDEAS convergence plot.

	Region I	Region II	Region III	Number of reactive separator flashes in G
Set 1	*1/16*	*1/16*	*1/8*	*60*
Set 2	*1/16*	*1/16*	*1/16*	*154*
Set 3	*1/32*	*1/32*	*1/32*	*561*
Set 4	*1/64*	*1/64*	*1/32*	*627*
Set 5	*1/128*	*1/64*	*1/32*	*903*

3.4. IDEAS process intensification results

The performance limits of reactive distillation networks are investigated by solving the optimization problem described in Eq. (36). Based on the previous section, a discretization level of 1/256, 1/128 and 1/32, for regions I, II and III respectively, is used to establish the IDEAS OP. Specifying $\alpha = 0.96875$ and $\beta = 0.0875$ as the region's edges, the 969 reactive flash separators are contained in the OP.

A reactor followed by an optimized separation system is used as a baseline to compare the results. The reactor outputs close to the equilibrium conversion, which is equal to 50% conversion of pentene for this reaction. The separation system is an IDEAS based network of flash separators (nonreactive). This baseline design is shown in Fig. 6.

The IDEAS results for different bounds in the total capacity, as well as the baseline value, are plotted in Fig. 7. The intensified reactive distillation network works with 5.5% of the baseline total reactive holdup for the same capacity value. The IDEAS based solution can also deliver a network with 15.7% of the baseline capacity for the same production rate and purity.

The IDEAS reactive distillation network results can also be compared with some of the reactive distillation solutions proposed in the literature. Nevertheless, values must be converted from the format originally presented to the total reactive holdup-total capacity space used in this work. Hoffmaster and Hauan (2006) presented two optimized reactive distillation columns, using single and multi-feed respectively. They presented both columns in a 20-stage design, detailed enough to convert the reactive holdup to kmol and to calculate the equivalent total capacity of the column. The Damköhler number was used to represent the dimensionless amount of reactive holdup. Hoffmaster and Hauan (2006) correlate the total amount of reactive liquid holdup H_T and the total Damköhler number Da_T according to the following equation:

$$\mathrm{Da}_T = \frac{k_{f,ref}}{F} H_T \tag{37}$$

The normal boiling point of 2-Pentene (310.08 K) is reported in the literature (Okasinski and Doherty, 1998; Chen et al., 2000; Hoffmaster and Hauan, 2006) as the reference temperature used in the calculation of the reference rate constant $k_{f,ref}$ for the metathesis case. Following the specifications of the study case, the system's total flowrate F is considered to be 100 kmol/h. The procedure and respective values used in the calculation of the equivalent reactive holdups and equivalent capacities for the referenced literature are detailed in the Appendix.

The residence time of 60 s (same as used in the IDEAS solution) was used to calculate the equivalent capacity of the non-reactive stages. Okasinski and Doherty's (1998) design is also presented in Hoffmaster and Hauan's paper for comparison. Since the pieces of information required to calculate the design's capacity are not available, for the sake of comparison Okasinski and Doherty's design is considered to have equal reactive holdup and capacity, which is the lowest possible value for the capacity variable. Finally, a design proposed by Jackson

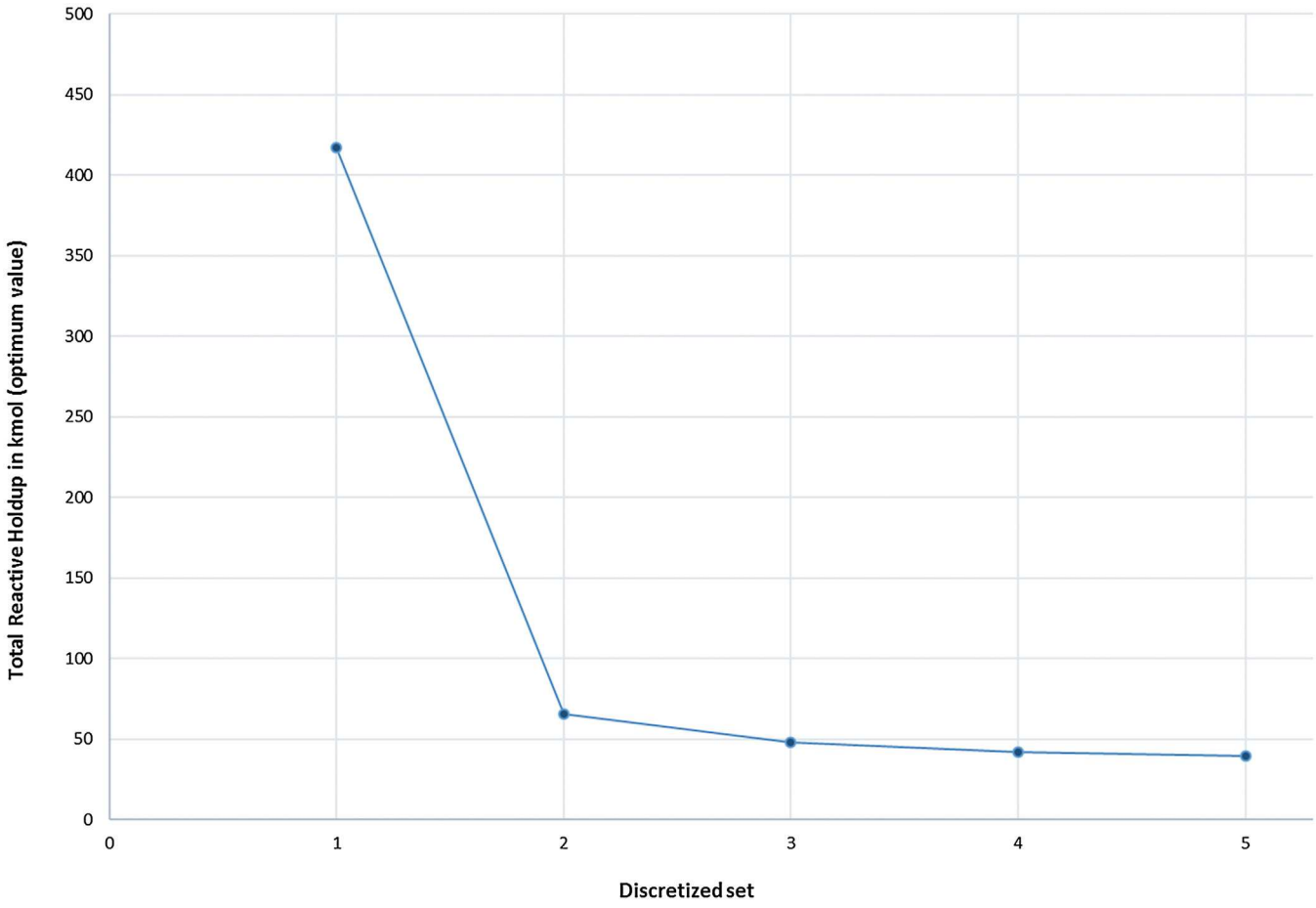

Fig. 5. IDEAS convergence for the metathesis of 2-Pentene with 87.5% purity, for minimum total reactive holdup.

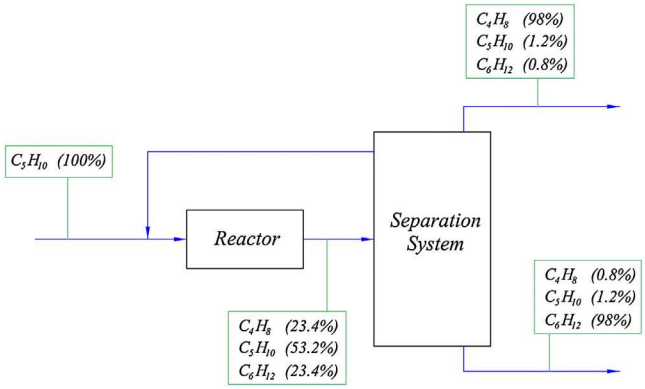

Fig. 6. A reactor followed by separation system used as baseline design for the metathesis of 2-pentene.

and Grossmann (2001), developed for minimum annualized cost, is also considered for comparison. This design has a slightly different purity target (95%) and inlet flow (120 kmol/h). Considering the conditions mentioned in this paragraph, the comparison is presented in Fig. 8.

Based on the identified performance limits, one can quantitatively assess the available design options with respect to this limit. For example, the reactor-followed-by-separation-system, used as baseline design, has a reactive holdup of 919.53 kmol, while the IDEAS based value for the same capacity is 47.48 kmol. Similarly, while the baseline utilizes 1,100.71 kmol as total capacity, the best IDEAS based value total capacity is 163.63 kmol. Thus, based on this baseline design, it is easy to verify that all proposed design solutions can be considered intensified. Moreover, optimized design solutions are evolving towards the IDEAS performance limits for this technology. Nevertheless, the

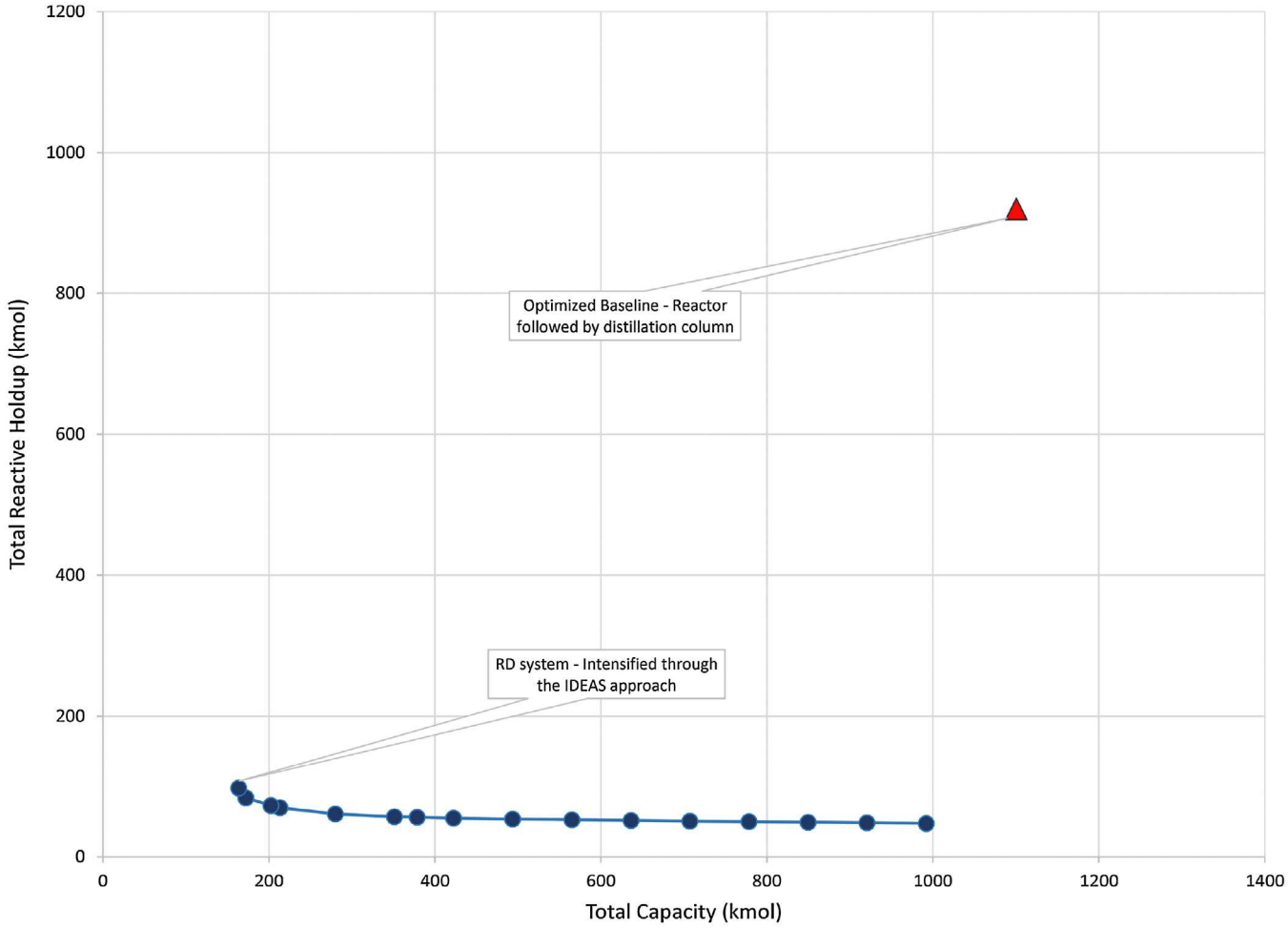

Fig. 7. Reactive holdup comparison between baseline and IDEAS designs as a function of total capacity.

results obtained from the application of the IDEAS framework show improvement opportunities in both the total reactive holdup (amount of catalyst used) and total capacity (equipment size, total flow) directions.

4. Conclusions

The Infinite DimEnsionAl Space State (IDEAS) framework is proposed as a process intensification tool in order to identify the performance limits of reactive separation processes. A model for the study of reactive distillation is developed using the IDEAS approach. The procedure leads to a linear convex problem formulation, in which the optimal solution is guaranteed to be global over all possible network configurations. The model was applied to investigate the use of reactive distillation for olefin metathesis. The case study features the metathesis of 2-pentene to form 2-butene and 3-hexene, an important chemical process for the oil industry. Total reactive holdup and total capacity, a surrogate for the amount of catalyst used and capital cost respectively, were selected as the system's variables of interest for process intensification. Using a traditional reactor-followed-by-separation-system scheme as a baseline, an intensified IDEAS based reactive distillation network can reduce the total reactive holdup and total capacity by 94.5% and 84.3% respectively. Results available in the literature were converted to the total holdup-total capacity space in the extent possible and compared with the IDEAS results. The comparison shows the existence of improvement potential, indicating that process intensification opportunities can be further explored in this reactive distillation system.

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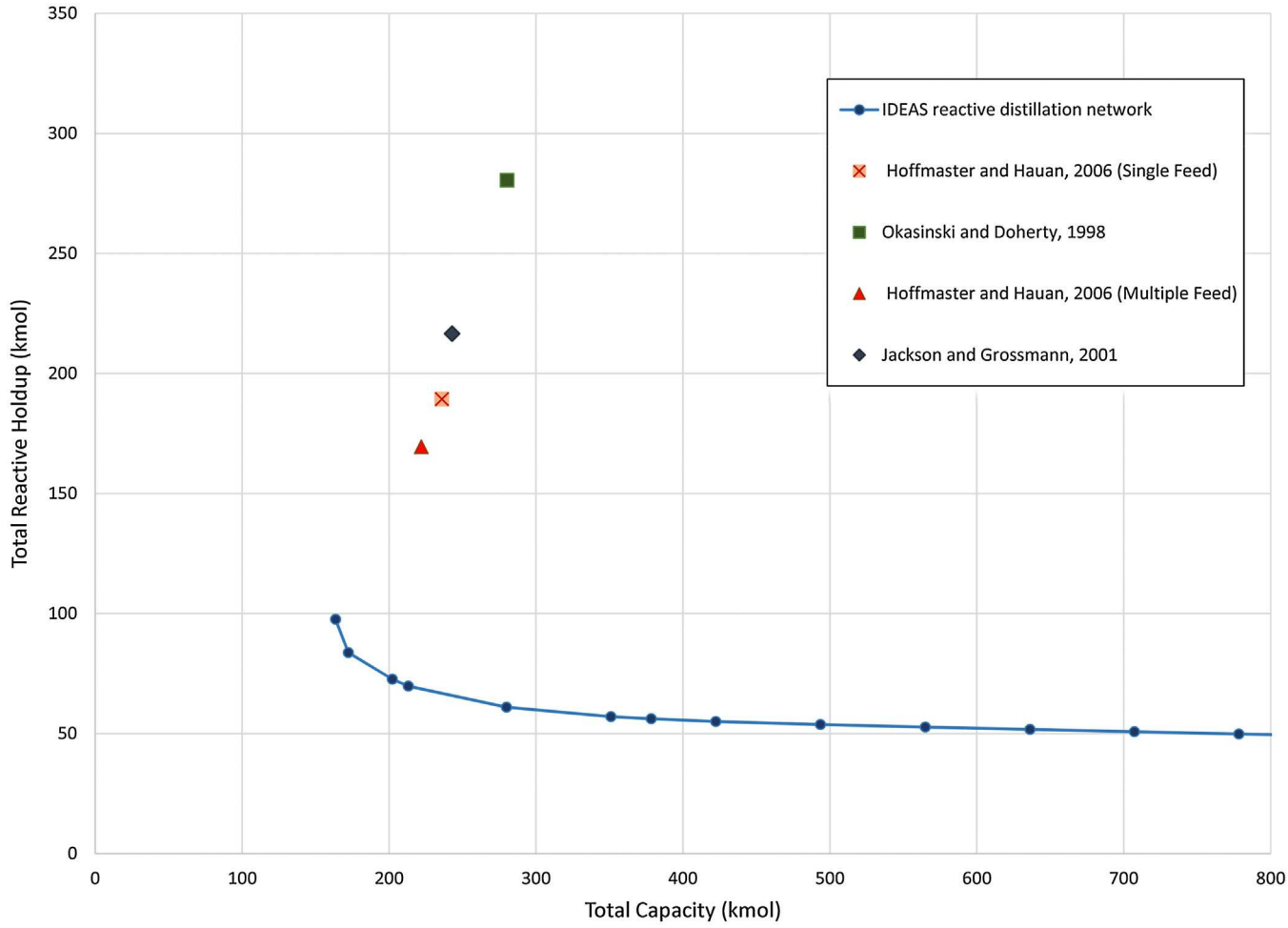

Fig. 8. IDEAS based performance limit for 2-Pentane metathesis (P = 1 bar) and comparison with literature.

Appendix A.

The detailed procedure and respective values used in the calculation of the equivalent reactive holdups and equivalent capacities for the referenced literature, represented in Fig. 8, are presented in this appendix. From Hoffmaster and Hauan (2006), the total amount of reactive liquid holdupH_T and the total Damköhler number Da_T are correlated by:

$$\mathrm{Da}_T = \frac{k_{f,ref}}{F} H_T \tag{A.1}$$

Since the kinetic model for the problem is already defined, if the temperature in which the reference rate constant $k_{f,ref}$ was calculated is known, it is possible to determine the total reactive holdup from the value of the total Damköhler number, for a given feed F.

According to Hoffmaster and Hauan, their results for the metathesis of 2-pentane were obtained using the same conditions as the design presented by Okasinski and Doherty (1998). Chen et al. (2000) also used the same specifications as Okasinski and Doherty (1998), explicitly declaring that the reference temperature used to calculate$k_{f,ref}$ is the normal boiling point of 2-Pentene (310.08 K).

The feed F used in this work's case study is equal to 100 kmol/h, as shown in Table 2. Considering this information, the total reactive holdup is determined from the Da_T presented in each of the reactive distillation systems presented in Fig. 8.

The value of the reactive holdup in each stage is calculated by using the total reactive holdup and the reaction distribution per stage, as shown in the referenced papers. The capacity for the specified residence time in each stage is also calculated, assuming constant molar overflow and considering the data presented in each of the cited references. For the reactive stages, the final value of the stage's capacity is either the capacity for the specified residence time or the reactive holdup for the stage, whichever is greater. This procedure is the same as adopted by the IDEAS methodology in the manuscript.

The values used in the reactive holdup and capacity calculations, in each of the referenced systems, are presented in Table A1. The distribution per stage of the reactive holdup and the stage's capacity based on the residence time are shown in Table A2–A5. In all these tables the roman characters represents the following systems:

- Hoffmaster and Hauan (2006) — Single Feed
- Hoffmaster and Hauan (2006) — Multiple Feed
- Okasinski and Doherty (1998)
- Jackson and Grossmann (2001)

Table A1
Values for the calculation of the referenced system's reactive holdup and capacities.

	I	II	III	IV[a]
Reflux ratio (dim)				
r	2	2	4	0.516
Flows (kmol/h)				
D	50	50	50	60*
F	100	100	100	120*
B	50	50	50	60*
Number of stages (dim)				
n	20	20	13	29
Feed stage (dim)				
Feed 1	11 (100%)	9 (75%)	7 (100%)	12 (28.6%)
Feed 2	–	14 (25%)		13 (30.6%)
Feed 3	–			17 (20.8%)
Feed 4	–			19 (20.0%)
Residence time (h)				
Tau	0.0166667	0.0166667	0.0166667	0.0166667
Total Reactive Holdup calculation – Eq. (A.1)				
Holdup (Da)	4.49	4.02	6.65	–
T_ref (C5) (K)	310.08	310.08	310.08	–
kf_ref (1/h)	2.3777348	2.3777348	2.3777348	–
Total Reactive Holdup (kmol)	***188.84***	***169.07***	***279.68***	***216.66***[a]

[a] This design has a purity target and inlet flow values of 95% and 120 kmol/h, respectively.

Table A2
Calculated capacity (per stage and total) for reactive distillation system I.

Stage	rxn/st	H	Tau*F	Capacity
1	0%	0.00	4.17	**4.17**
2	0%	0.00	4.17	**4.17**
3	0%	0.00	4.17	**4.17**
4	0%	0.00	4.17	**4.17**
5	1%	1.89	4.17	**4.17**
6	2%	3.79	4.17	**4.17**
12	10%	18.94	5.83	**18.94**
13	10%	18.94	5.83	**18.94**
14	9%	17.04	5.83	**17.04**
15	6%	11.36	5.83	**11.36**
16	1%	1.89	5.83	**5.83**
17	0%	0.00	5.83	**5.83**
18	0%	0.00	5.83	**5.83**
19	0%	0.00	5.83	**5.83**
20	0%	0.00	5.83	**5.83**
		Total Capacity =		**235.95**

Table A3
Calculated capacity (per stage and total) for reactive distillation system II.

Stage	rxn/st	H	Tau*F	Capacity
1	0%	0.00	4.17	**4.17**
2	0%	0.00	4.17	**4.17**
3	0%	0.00	4.17	**4.17**
4	0%	0.00	4.17	**4.17**
5	0%	0.00	4.17	**4.17**
6	1%	1.70	4.17	**4.17**
12	16%	27.13	6.25	**27.13**
13	15%	25.43	6.25	**25.43**
14	10%	16.95	6.25	**16.95**
15	4%	6.78	5.83	**6.78**
16	0%	0.00	5.83	**5.83**
17	0%	0.00	5.83	**5.83**
18	0%	0.00	5.83	**5.83**
19	0%	0.00	5.83	**5.83**
20	0%	0.00	5.83	**5.83**
		Total Capacity =		**222.01**

Table A4
Calculated capacity (per stage and total) for reactive distillation system III.

Stage	rxn/st	H	Tau*F	Capacity
1	7.69%	21.57	7.50	**21.57**
2	7.69%	21.57	7.50	**21.57**
3	7.69%	21.57	7.50	**21.57**
4	7.69%	21.57	7.50	**21.57**
5	7.69%	21.57	7.50	**21.57**
6	7.69%	21.57	7.50	**21.57**
12	7.69%	21.57	9.17	**21.57**
13	7.69%	21.57	9.17	**21.57**
		Total Capacity =		**280.45**

Table A5
Calculated capacity (per stage and total) for reactive distillation system IV.

Stage	rxn/st	H	Tau*F	Capacity
Cond.	0%	0.00	2.03	**2.03**
27	0%	0.00	2.03	**2.03**
26	0%	0.00	2.03	**2.03**
25	6.25%	10.32	2.03	**10.32**
24	6.25%	10.32	2.03	**10.32**
23	6.25%	10.32	2.03	**10.32**
17	6.25%	10.32	2.85	**10.32**
16	6.25%	10.32	2.85	**10.32**
15	6.25%	10.32	2.85	**10.32**
14	6.25%	10.32	2.85	**10.32**
13	6.25%	10.32	3.46	**10.32**
12	6.25%	10.32	4.03	**10.32**
11	6.25%	10.32	4.03	**10.32**
10	6.25%	10.32	4.03	**10.32**
9	6.25%	10.32	4.03	**10.32**
8	6.25%	10.32	4.03	**10.32**
7	6.25%	10.32	4.03	**10.32**
6	6.25%	10.32	4.03	**10.32**
5	6.25%	10.32	4.03	**10.32**
4	0%	0.00	4.03	**4.03**
3	0%	0.00	4.03	**4.03**
2	0%	0.00	4.03	**4.03**
1	0%	0.00	4.03	**4.03**
Reb.	0%	0.00	4.03	**4.03**
		Total Capacity =		**242.92**

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