Flexibility and environmental assessment of process-intensified design solutions: A DWC case study

Alessandro Di Pretoro, Matteo Fedeli, Flavia Ciranna, Xavier Joulia, Ludovic Montastruc, Flavio Manenti

Flexibility and Environmental Assessment of Process-intensified Design Solutions: a DWC Case Study

Alessandro Di Pretoro[a,b], *Matteo Fedeli*[a], *Flavia Ciranna*[a], *Xavier Joulia*[b], *Ludovic Montastruc*[b*], *Flavio Manenti*[a]

[a]Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica «Giulio Natta», Piazza Leonardo da Vinci 32, 20133 Milano, Italy

[b]Laboratoire de Génie Chimique, Université de Toulouse, CNRS/INP/UPS, Toulouse, France

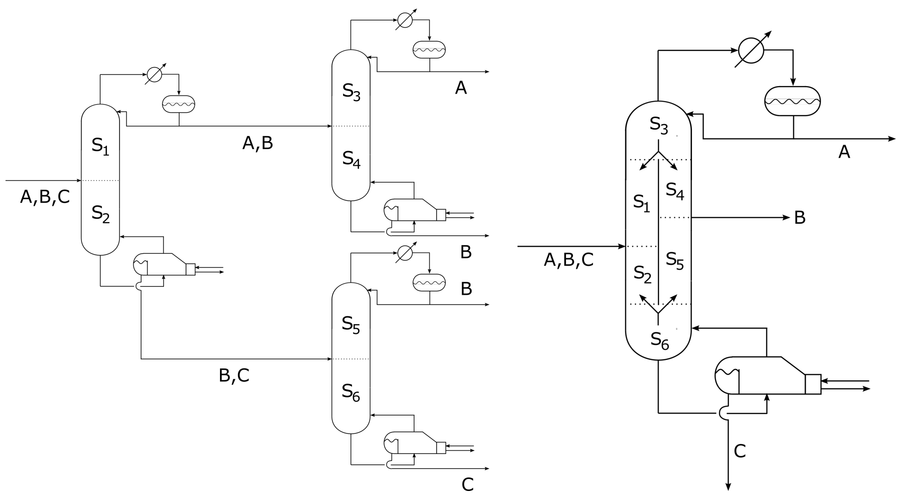
Abstract

During the last decades, energy and process integration have become the most spread practices to optimize chemical processes both from economic and environmental perspectives. While the design of the integrated and conventional configurations are usually compared by referring to nominal operating conditions, assessing the implications of process integration on system flexibility could be of critical importance, especially when considering the uncertain nature of renewables. This paper aims then at the comparison of different integrated and conventional unit design performances under uncertain conditions by means of a biorefinery Acetone-Butanol-Ethanol separation case study. An indirect distillation train and different configurations of Dividing Wall Column have been designed and compared to assess the environmental and economic advantages for different flexibility ranges. The proposed methodology allows to select the most suitable configuration for the required performance and to have more conscious expectations about investment costs and emissions when flexibility is taken into account.

Highlights:

1. Process intensified solutions results to be more profitable and sustainable but their design is usually optimized with respect to nominal operating conditions only.
2. In case of biomass based processes, accounting for external deviations is of critical importance due to the feedstock nature fluctuations over the seasons.
3. A preliminary flexibility assessment during the design phase allows to identify the best design configuration corresponding to different flexibility requirements.

Keywords: DWC, flexibility, GWP, optimal design, process integration, ABE.



(a) Distillation train (b) Dividing Wall Column

Fig. 1: Conventional vs intensified distillation

1 Introduction

During the last decades, process intensification has become the best practice in chemical engineering due to the need of more effective and profitable equipment nad operations as well as to the concerns related to the CO_2 emissions associated to energy demanding processes [1].

Process intensification is defined by Stankiewicz & Moulijn (2000) [2] as the analysis of two main areas:

- process-intensifying equipment, such as novel reactors, and intensive mixing, heat-transfer and mass-transfer devices;
- process-intensifying methods, such as new or hybrid separations, integration of reaction and separation, heat exchange, or phase transition (in so-called multifunctional reactors), techniques using alternative energy sources (light, ultrasound, etc.), and new process-control methods (like intentional unsteady-state operation).

Obviously, these areas are strongly interrelated since new methodologies may involve innovative types of equipment to be designed and vice versa, while already developed novel units make often use of new, unconventional processing methods.

Among the separation processes in process industry the distillation is by far the most common one and the most energy demanding as well. Several design alternatives have been proposed in literature in order to make the standard distillation column more effective. The most widely used is the Heat Pump Assisted Distillation (HPAD) column taking advantage of a vapor recompression cycle in order to save about one third of the energy demand [3, 4].

The conventional distillation trains for multicomponent mixtures purification have been replaced by the most compact and effective Dividing Wall Column (hereafter DWC) as shown in Figure 1 where the S_i numbers correspond to the equivalent sections. In recent years this intensified distillation unit has been considered the best practice in case of multicomponent mixture separation since, among all those non-standard configurations, it is the only large-scale process intensification case where both capital and operating costs as well as the required installation space has been drastically reduced [5].

The idea of intensified distillation column configuration was first introduced by Petlyuk in 1965 [6] as the connection between a prefractionator and a standard column with condenser and reboiler. In particular, the Dividing Wall Column represents the Petluk column configuration arrangement in a single column shell [7].

The analysis of the process characteristics corresponding to intensified solutions that perform better than the classical sequence of standard columns has been widely discussed [8, 9] and resulted in a set of well-established conditions collected and analyzed by Petlyuk in its work [10]. Moreover, several procedures for the DWC design have been proposed in literature during the last decades both with shortcut methods [11, 12, 13] and detailed optimization algorithms [14, 15, 16, 17].

All those research studies confirm the higher profitability and sustainability of the DWC alternative with respect to the classical distillation train. However, all those analyses are strictly related to nominal operating conditions, i.e. they do not account for process intensification and external disturbances at the same time. If those design solutions can be suitable for refinery related applications, for which the properties of treated stream can be considered almost stable, in case of bio-processes neglecting the intrinsic variable nature of the feedstock during the year seasons could be rather restrictive.

In the light of all those remarks, a flexibility analysis could be then a tool of critical importance to have a preliminary estimation of process integration implications on the system performances over an uncertain operating conditions range during the design phase. Design and uncertainty and design for flexibility are well-established research fields in the Process System Engineering (PSE) domain.

In particular, flexibility is defined as the ability of a process to accommodate a set of uncertain parameters [18]. Several flexibility indexes both deterministic [19, 20] and stochastic [21, 22] have been proposed in literature by several authors. Their detailed comparison on a distillation column case study can be found in a publication by Di Pretoro et al. (2019) [23].

In particular, in this paper, the two most common deterministic flexibility indexes will be used, namely the Swaney and Grossmann F_{SG} flexibility index [19] and the Resilience Index RI proposed by Saboo and Morari [20]. Their detailed formulation is later discussed in the corresponding section 3.2. However, the proposed approach is not limited to deterministic indexes since the same analysis could be conducted with stochastic ones whether a probability distribution function for the uncertainty characterization were available.

In particular, as already presented in previous studies [23, 24], flexibility analysis can be coupled with the economics in order to have a rigorous assessment of the additional investment costs related to a more flexible unit and to verify the higher profitability of a process intensified configuration with respect to the standard distillation train.

Due to the current concern about environmental impact, the same procedure can be applied by coupling flexibility analysis and CO_2 emissions quantification

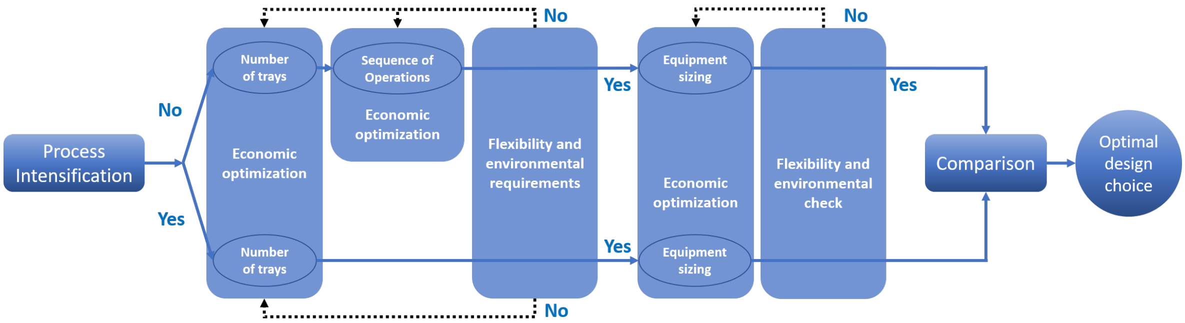


Fig. 2: Multi-criteria design steps sequence for process intensified units

in order to have a more reliable assessment about the real sustainability gap between DWC and the conventional column sequence under uncertain operating conditions.

In addition to the comparison between the two different process configurations, the flexibility based design can be applied to define other important process parameters for intensified units, such as the optimal number of stages N for the Dividing Wall Column. In fact, the number of equilibrium stages for each column section are the design parameters that uniquely define the DWC unit while equipment sizing and vapor and liquid split ratios are function of operating conditions. For this reason, beside the optimal DWC layout under nominal operating conditions, the system behaviour under uncertainty will be assessed for separation units with a lower and a higher N as well both from an economic and an environmental perspective. In fact, for a given Total Annualized Cost (TAC), different expenses distribution between OPerating and CAPital EXpenses (OPEX and CAPEX respectively) could result in different equivalent CO_2 emissions. In particular, higher investments could allow a lower external duties demand in case process variables perturbations should be compensated with a corresponding utility management.

The final goal of this study is then the comparison between equivalent conventional and intensified solutions by combining flexibility, economic and environmental analyses in a more complete design procedure. This new tool will allow the decision maker to have a more conscious overview of the design alternatives within a range of operating conditions wider than the nominal ones.

In the context of the general design procedure, starting from the feasibility assessment to the validation of the unit operation dynamics for the selected control strategy, the analysis and results provided in this research study focuses on the equipment optimal design step. A detailed insight of the economic, flexibility and environmental-based design steps performed in this study for the comparison between conventional and intensified separation units is provided in Figure 2.

The multi-criteria design optimization problem has been broken down into a sequence of steps for the conventional and intensified units respectively. Some iterative loops are included whether the previous design choice needs to be reconsidered in the light of flexibility or environmental requirements. Although the process intensified design path might look smoother, the complexity of simulta-

Component\Property	Value	Unit
Acetone	12.030	mol/s
n-Butanol *	61.328	mol/s
Ethanol	3.839	mol/s
Water *	12.428	mol/s
Pressure	101.325	kPa
Temperature	361.26	K

Tab. 1: Feed properties

neous equilibrium stages and sections layout optimization for the integrated unit sections implies the solution of a much more complex mathematical problem as discussed in a previous publication and better detailed in the corresponding section 3.1.

The comparison between the optimal distillation train and DWC design solutions is then carried out based on both economic and environmental indicator accounting for uncertain operating conditions. Therefore, the final choice is not only of economic or environmental indicators but, more importantly, it also reflects the combination between the expected deviation nature and the flexibility requirements of the specific design problem.

2 The ABE mixture case study

The case study presented in this paper to analyze the implications of process intensification on process performances under perturbed operating conditions is an ABE/W (Acetone-Butanol-Ethanol/Water) mixture separation.-The flexibility assessment for the conventional distillation train configuration was already provided by Di Pretoro et al. (2020)[24] and will serve as a reference for the DWC one.

There are two main reasons that make this example particularly suitable for the purpose of this study. First, the limitations related to the non-ideal thermodynamic behaviour of the mixture to be processed that imply the presence of separation feasibility boundaries that should be taken into account as constraints during the flexibility assessment. Second, the renewed interest in bioprocesses from a sustainability perspective and biofuels in particular as recently discussed in the International Energy Agency yearly report [25]. In fact, biomass based operations need to account for their volatile nature and, thus, their lower environmental impact should be proved over the entire operation range and not only in correspondence of a particular operating condition. Accordingly, the higher sustainability of renewables and green feedstocks should not be compromised by an exponential energy demand increase for the intensified configuration when perturbations are likely to occur.

As reported by several studies concerning different bacterial strains, the ABE/W fermentation suffers from product inhibition [26], that means there is a n-butanol threshold beyond which the bacteria are poisoned by the same fermentation product. For this reason the fermentation broth is rich in water that should be preliminary removed according to one of the processes proposed in literature such as pervaporation [27], liquid-liquid extraction [28] etc.. Due to its high latent heat indeed such a huge amount of water would be very expensive to be treated during the pure components purification phase, in particular if the product purification is carried out by an energy demanding process such as distillation.

On the one hand then, there's the need to describe the oscillations in the butanol yield downstream the fermentation process related to the feedstock seasonality and to the selected bacterial strain; on the other hand, the description of the dewatering section performances and its eventual malfunctioning should be accounted for.

Therefore, in the light of these premises, the water and n-butanol content in the feed streams were selected as uncertain variables for this separation process case study. Moreover, the amount of water and butanol in the mixture are critical parameters from a thermodynamic perspective because of the feasibility constraints related to the butanol-water heteroazeotrope.

The feed properties are listed in Table 1. As already discussed by Di Pretoro et al. (2021)[29], at least n-butanol and acetone should be recovered for the profitability of the process. Therefore the process specifications are as follows:

- Acetone:
    1. Recovery ratio in the distillate: 0.985;
    2. Mass fraction in the distillate: 0.995;
- n-Butanol:
    1. Recovery ratio in the bottom product: 0.9604;
    2. Mass fraction in the bottom product: 0.990;

In practice the DWC side stream has the same purpose of the second column bottom product in the indirect distillation train, i.e. the removal of a water-ethanol rich stream that could be optionally sent to a further purification process after a more accurate quantification of the additional ethanol recovery profitability.

The thermodynamic flexibility analysis of the same distillation process was already carried out by Di Pretoro et al. (2020) [30]. The physical feasibility boundaries indeed do not depend on the affordable investment but just on the mixture properties and process specifications. This preliminary analysis of the thermodynamically feasible domain has then the purpose to outline the maximum flexibility values that can be achieved when neglecting "weaker" constraints such as profitability, controllability and safety.

The thermodynamic model used for process simulation is the Non-Random Two Liquids described in detail in Appendix B. It is able indeed to correctly predict Vapor-Liquid and Liquid-Liquid Equilibrium and, in particular, homogeneous and heterogeneous azeotropes as already discussed by several authors [7, 24, 28, 30, 31, 32].

Due to the low amount of ethanol and to the lack of interest in its purifications, the water-ethanol azeotrope does not affect the process feasibility. On the contrary, even though the operating conditions are always far from LLE region, the water-butanol azeotrope is a saddle point and defines a distillation boundary according to the Residue Curve Mapping [30]. In case of high water content in the feed then the minimum amount of n-butanol lost in the water rich stream because of water-butanol interactions becomes considerable and endangers the butanol recovery specification.

Further details about the DWC column design, process simulation and performances under uncertain operating conditions are commented in the following section.

3 DWC design and flexibility assessment

The purpose of this section is to provide the detailed description of methods and tools that have been used for the DWC design and simulation as well as for the related flexibility assessment.

In particular, the first section addresses the DWC design problem in general and presents the obtained results under nominal operating conditions. On the other hand, the second section provides the mathematical formulation of the indexes that will be used for the flexibility assessment in order make the results presented section 4 clearly understandable.

3.1 DWC design

In the last years the Dividing Wall Column optimal design procedure has been a topic of major concern in the Process System Engineering domain. The main complication with respect to the equivalent sequence of standard distillation columns is related to the higher number of degrees of freedom to be fulfilled at the same time for all the column sections due to the impossibility to optimize them in series as for the distillation train.

However, the effort worthiness has been largely proved in literature since the DWC allows on average the 30% savings both from an economic and an equivalent CO_2 emissions point of view and implies a considerable installation space reduction as well as a lower amount of instrumentation needed with respect to two (or three) columns.

Several design procedures were proposed in literature including a wide range of computational tool for the design optimization such as the rigorous solution of the Mixed Integer NonLinear Programming (MINLP) problem by using a superstructure [14, 17], the employment of genetic algorithms [28] and stochastic optimization strategies [33, 34, 35]. Among them, some research work for the ABE mixture can be found as well under nominal operating conditions [28, 31, 32].

As already discussed, the DWC design configurations under nominal operating conditions used for the flexibility assessment are those obtained for the same case study by Di Pretoro et al. (2021) [29] with a feasible path-based procedure. Starting from a column layout and streams initialization provided by the DWC shortcut module in ProSimPlus® process simulator [36], equilibrium stages are added and removed in each column section based on a concentration profile analysis until the lowest Total Annualized Cost for a converging simulation is obtained.

In particular, the study of this paper accounts for three different DWC configurations: the 42 stages configuration whose TAC was found to be the lowest one, a second column with a lower number of stages (37) and a third column

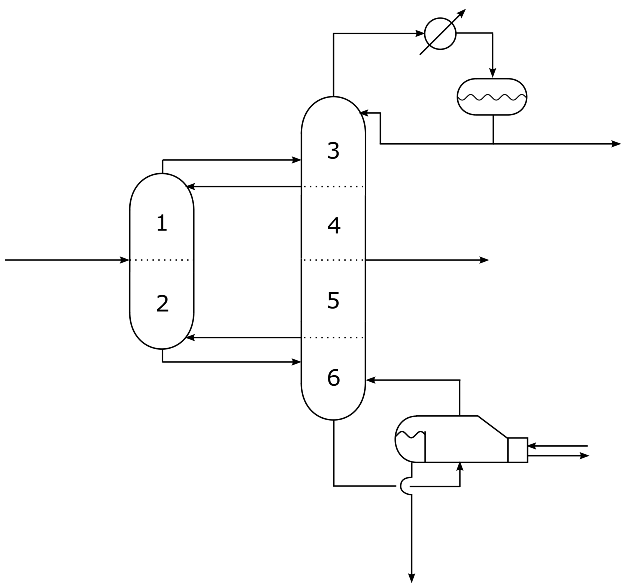


Fig. 3: Two-column model (Petlyuk)

with a higher number of equilibrium stages (52). The fact that the 42 stages column resulted the optimal configuration under nominal operating conditions indeed doesn't imply that it is still the most profitable solution when taking into account the feed perturbations as well. According to the relationship between investment and operating costs, a higher number of stages indeed could mitigate the required duty response to the external perturbations.

On the other hand, the design of the distillation train for the same separation process was already performed and optimized with respect to nominal operating conditions by Di Pretoro et al. (2020) [24] and its flexibility assessment with different flexibility indexes is already carried out in the same paper. The indirect configuration resulted to be the most profitable and flexible due to the removal of bio-butanol first that is the most abundant component in the feed downstream the preliminary dewatering process.

The main inconvenient for the DWC process simulation is the absence of dedicated modules in commercial process simulators. The DWC can be nevertheless simulated thanks to thermodynamic equivalent configurations [37] made up of more simple columns connected to each other. There are three most common alternative layouts for a DWC that are namely the pump-around model, the two-column model also referred to as the Petlyuk column configuration and the four-column model.

In this study, the Petlyuk configuration shown in Figure 3 will be employed since it results the best compromise between number of units and interlinking streams to be initialized for the simulation convergence. Moreover, it is the configuration for which the shortcut design provides all the required data without the need of equivalent conversions and the same layout used to perform the design under nominal operating conditions.

The interlinking streams reflect as well the two degrees of freedom related to the liquid and vapor splits that are manipulated in the flexibility analysis in order to meet the process specifications when operating conditions change. In particular, when the reflux ratio varies to keep the separation effective, the liquid split is constrained by the product specification while vapor split is adjusted in order to minimize the heat duty consumption as discussed in detail in Waltermann et al. (2019)[17]. As concerns the design variables accounted for in the flexibility assessment, they are namely the column diameter (and thus the wall position), the condenser and reboiler heat transfer surfaces and, finally, the number of stages as later discussed in more detail.

The streams initialization is valid for the first iteration, after that the sensitivity analysis tool is used to carry out the flexibility assessment and the first guess value of each step is based on the results achieved in the previous iteration.

ProSimPlus® process simulator was used for the shortcut design and interlinking streams initialization while the process simulation for the equipment design and for the flexibility assessment was carried out by means of AVEVA SimCentral® process simulator.

3.2 Flexibility indexes

Flexibility indexes are the main tool exploited in this research study to discuss the impact of process intensification on the system performances under perturbed operating conditions. These indicators are particularly useful since they can be coupled with other system related variables, as it will be later shown for costs or emissions, in order to outline their response to a set of parameters deviations. Moreover, with respect to the sensitivity analysis, that provides the response of a dependent variable for a perturbation of an independent one, the flexibility index allows to synthesize in a single number the system performances under uncertain conditions whatever the dimension of the uncertain domain.

The several flexibility indexes that can be found in literature differ from each other according to the way uncertainty is taken into account for their calculation. In this article, two deterministic flexibility indexes will be used, since the main purpose is to correlate the impact of the deviation magnitude on TAC and CO_2 emissions.

The first, and most popular one, is the Swaney and Grossmann F_{SG} flexibility index [19]. It is defined as the maximum fraction of the expected deviation of all the uncertain variables at once that can be accommodated by the system and its mathematical formulation stands as:

$$F_{SG} = \max \delta \tag{3.1}$$

$$s.t. \max_{\theta \epsilon T(\delta)} \min_{z} \max_{j \epsilon J} f_j(d, z, \theta) \leq 0 \tag{3.2}$$

where, given θ^N as the nominal vector of the uncertain parameters and $\Delta\theta^+$ / $\Delta\theta^-$, the expected deviations in the positive and negative direction respectively, $\Theta(\delta)$ is the hyper-rectangle described by the equation:

$$\Theta(\delta) = \{\theta : \theta^N - \delta \cdot \Delta\theta^- < \theta < \theta^N + \delta \cdot \Delta\theta^+\} \tag{3.3}$$

and d and z are the design and the control (i.e. manipulated) variables respectively. It geometrically represents, the maximum scaled-up hyper-rectangle that can be inscribed inside the feasible region as shown by the blue line in Figure 4.

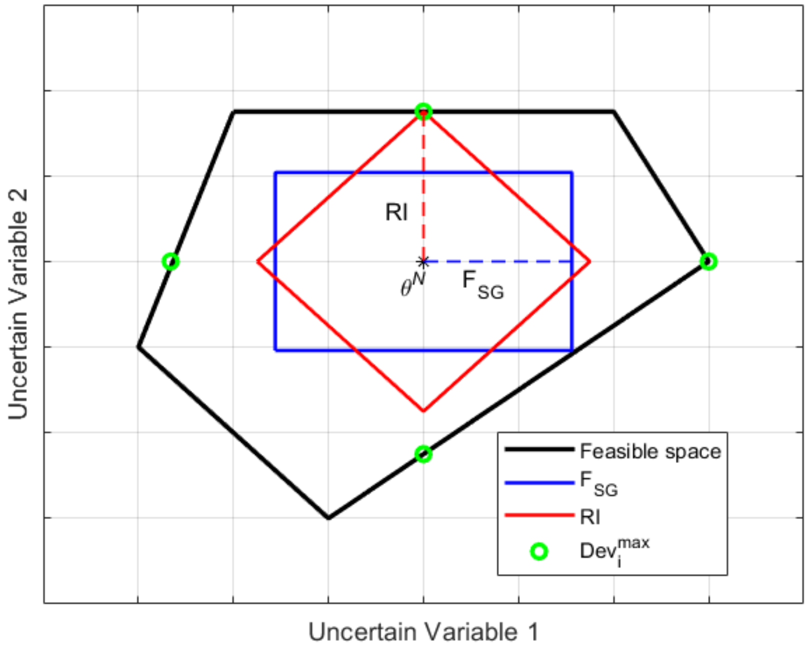


Fig. 4: Flexibility index (F_{SG}) vs Resilience Index (RI)[23]

The other flexibility index considered in this article is the so called Resilience Index RI proposed by Saboo and Morari [20]. It is defined as the largest total disturbance load, independent of the direction of the disturbance, that a system is able to withstand without becoming unfeasible. It mathematically stands as:

$$RI = \underset{i}{max}\, \Delta\theta_i^{\pm} \tag{3.4}$$

$$s.t. \{\underset{j}{\max} f_j(\theta) \leq 0,\ \forall \Delta\theta : \sum_i |\Delta\theta_i| \leq RI\} \tag{3.5}$$

It geometrically represents, the largest maximum scaled-up polytope that can be inscribed inside the feasible region as shown by the red line in Figure 4.

In the application of these two indicators to the ABE case study, two process parameters have been considered as uncertain, namely the water and n-butanol partial flowrates respectively. As previously commented, they reflect the impact of product perturbations in the upstream fermentation and the inefficiency of an underperforming dewatering section. Moreover, considering the partial flowrates of the two most abundant species instead of the feed composition allows the analysis with respect a third uncertain parameter as well: the total feed flowrate, i.e. the unit capacity.

The reason why more than one flexibility index is usually employed for the flexibility analysis is to analyze different properties of the system. In particular, in this case, the Resilience Index allows to detect which is the maximum allowed deviation for each single uncertain parameters and which one among them is the most constraining. On the other hand, the F_{SG} index allows to assess the impact of simultaneous deviations from an economic or environmental perspective. As discussed in Di Pretoro et al.(2019)[23], since in this study the flexible design problem is addressed, the results are provided for a flexibility index range instead of providing a single index value for a given design as in the flexibility index problem. For this reason, the indexes are expressed as a percentage of the variables nominal value, that corresponds to considering the expected deviation equal to the 100% of it.

In particular, since there is no reason to preliminary assume that the feasible space is convex, the calculation is performed over the entire rectangle or polytope characterized by the related index and the most conservative design solution (i.e. largest equipment sizing) as well as the highest value of CO_2 emissions allowing to operate over the whole region are considered.

In the next section the flexibility analysis results will be presented following the order economic (F_{SG} - RI index) and environmental (F_{SG} - RI index) assessment.

4 Results

The results of both the flexibility and the environmental assessments are reported and discussed in the corresponding subsections here below. In particular, the interpretation of the obtained trends from a decisional point of view, according to the expected deviation magnitude and process requirements, are commented in detail.

In the following plots, results will be presented for three relevant DWC configurations with different number of stages. In fact, as discussed in section 3.1, the convergence of the DWC unit simulation represents a critical issue and the flexibility analysis over the whole range of perturbations was not possible for a continuous variation in the number of stages. For this reason, the optimal number of stages for each of the column sections was optimized first and, then, the flexible equipment sizing (i.e. column diameter, condenser and reboiler heat transfer surface etc.) was scaled in line with the applied deviation according to the design steps already presented in Figure 2.

These three configurations with 37, 42 and 52 stages respectively, are those who better performed in terms of convergence of the simulation over the entire uncertain domain. To be more precise, the 42 stages configuration is the optimal one under nominal operating conditions while the other two represent with good accuracy the effect of a number of stages under- or over-sizing from a flexibility point of view.

4.1 Flexibility assessment

The flexibility assessment was successfully carried out for the different DWC configurations. The same thermodynamic limitations highlighted by Di Pretoro et al. (2020) [30] have been found with process simulations both for the Swaney and Grossmann flexibility index F_{SG} and for the Resilience Index RI. In particular, the feasibility boundary has the same quasi-linear trend for a constant water/butanol flowrate ratio equal about to 0.225 [24].

Figure 5 shows the Total Annualized Costs sensitivity analysis results for the optimal configuration under nominal operating conditions (i.e. 42 stages) with respect to both water and butanol partial flowrate deviations. To be more precise the reported costs have been normalized with respect to the nominal operating conditions one and calculated according to the Guthrie-Ulrich-Navarrete correlations [38, 39, 40, 41] described in detail in the corresponding Appendix C. It is worth precising that the jagged shape of the feasibility boundary (high water and low n-butanol content) is simply due to the discretization of the uncertain domain.

The most important outcome of the sensitivity analysis is the direction of higher costs increase. First of all, it can be noticed that both the uncertain parameters strongly affect the operation TAC. In particular, differently from ideal separation processes, the cost increase direction does not correspond to the higher capacity requirements, i.e. positive deviation of the two flowrates. This behaviour can be detected when the operation approaches the thermodynamic feasibility boundary, i.e. when more severe operating conditions required to compensate the more difficult separation.

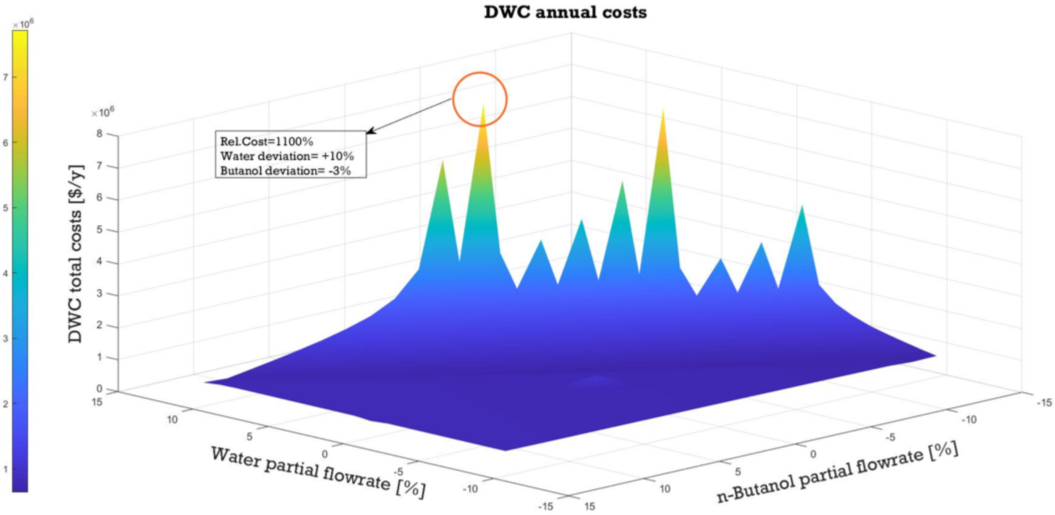
When the feed butanol content decreases and the water flowrate increases the separation indeed becomes more challenging due to the difficulty to satisfy the process specifications related to the butanol recovery and purity. The manipulated variable mainly affected by this disturbance is the reflux ratio. Its increase results not only in a more considerable reboiler heat and condenser cooling duties but also in higher investment costs due to a larger column diameter, needed to avoid flooding when higher flowrates are circulating in the column, as well as a more relevant heat transfer surface areas both for reboiler and condenser in order to ensure an effective heat transfer.

The TAC increase from the nominal operating point towards the feasibility boundary has an exponential trend resulting in a more and more expensive unit as the water/butanol ratio becomes higher. It achieves about twelve times the nominal costs in the proximity of the unfeasible region.

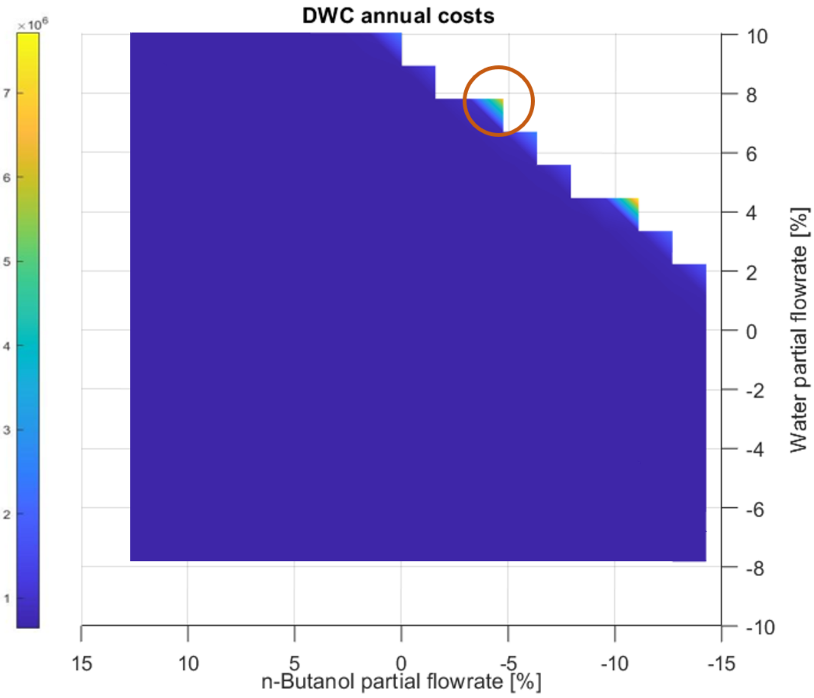
To switch from the sensitivity to the flexibility analysis, the index corresponding to the property of interest should be used in order to correlate the equipment design with the flexibility requirement. This procedure was discussed in detail by Di Pretoro et al. (2019) [23] and allows to outline an "additional costs vs. flexibility" decisional plot based on the equipment oversizing and related investment costs required to deal with perturbed conditions.

Figure 6 shows the required additional costs for a given Swaney and Grossmann flexibility index F_{SG} for the three DWC configurations. These values are normalized with respect to the optimal solution under nominal operating conditions, i.e. 42 stages column (blue trend in correspondence of 0 % deviation). First of all it can be noticed that all the curves follow an almost linear trend for low flexibility values while they progressively increase when approaching the thermodynamic flexibility boundary where the slope becomes much steeper. In particular, this sudden increase in the unit additional costs is observed first in the configuration with a lower number of equilibrium stages while it occurs later for oversized distillation columns.

On the one hand, the 37 stages DWC always results (red) less profitable than the 42 stages one and the presence of external disturbances emphasizes even more this gap. On the other hand, even though under nominal operating conditions the 42 stages DWC results more profitable than the 52 stages one (green), there exists a given flexibility value ($F_{SG} = 3.8\,\%$ and $RI = 7\,\%$) after which the two curves cross each other and the presence of additional stages is able to mitigate the external perturbations and to reduce the reflux ratio



(a) Side view



(b) Top view

Fig. 5: DWC total costs vs uncertain domain

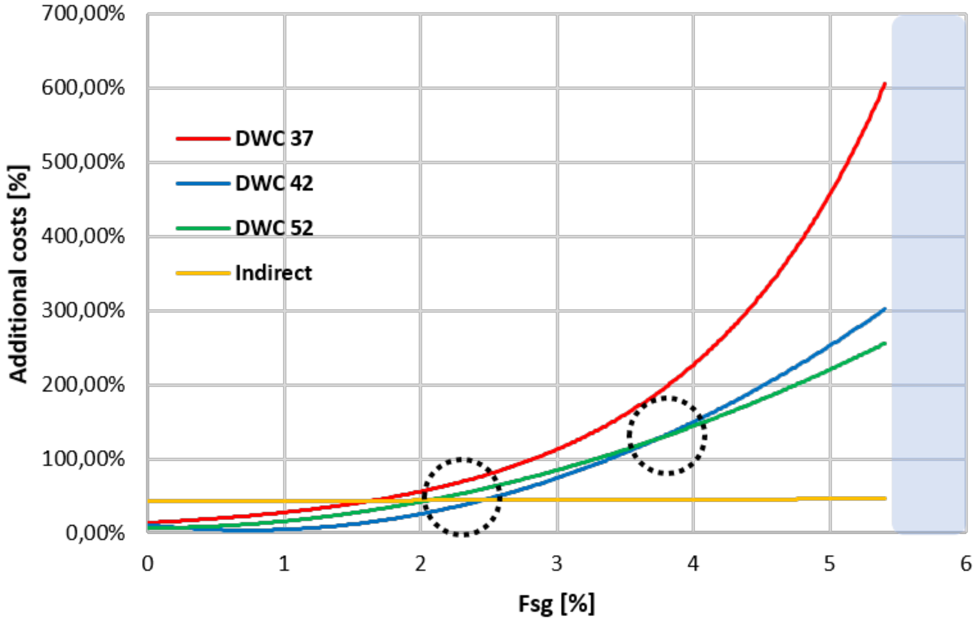


Fig. 6: Additional costs vs Flexibility (F_{SG})

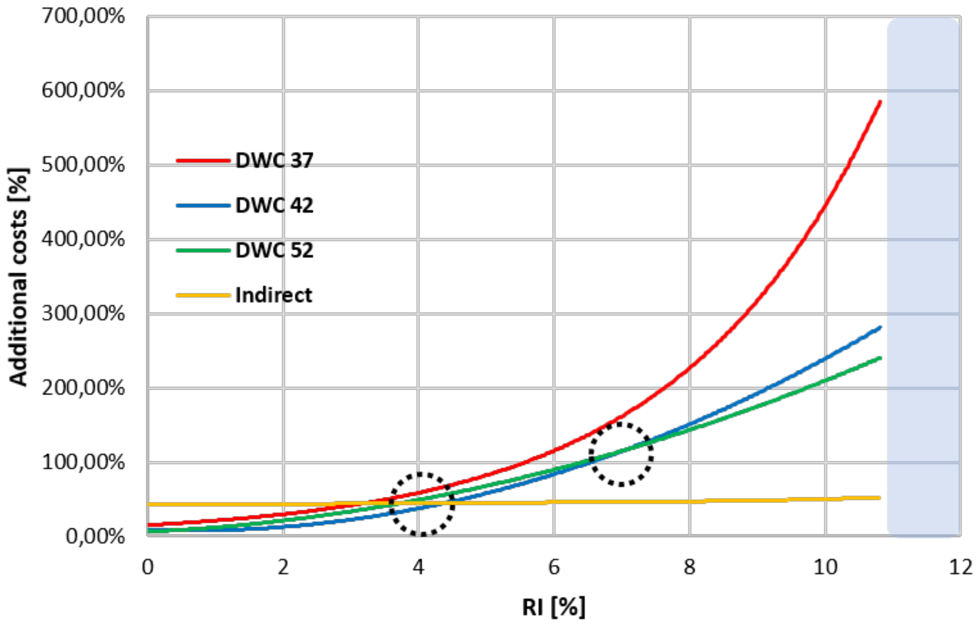


Fig. 7: Additional costs vs Flexibility (RI)

required to withstand them.

Therefore, when accounting for uncertain operating conditions, the optimal design configuration cannot be uniquely defined but it strictly depends on the expected deviation range and on its likelihood.

In the same Figure 6 the comparison between the conventional indirect configuration train (yellow) and the process intensified solutions can be observed. As it can be noticed, the DWC allows to save about 30 % of the total annual costs with respect to the series of columns under nominal operating conditions. However, the additional costs required to achieve a desired flexibility index value increase much more slowly with respect to the dividing wall column causing the two configurations to have the same TAC at about $F_{SG} = 2.5\,\%$.

This behaviour is due to the fact that, in case of columns sequencing, the first column of the indirect configuration, aimed at the preliminary n-butanol recovery, is the one responsible for the main compensation of the external disturbances. As a consequence, the conventional distillation train requires results minor changes on the equipment sizing while, in case of process intensification, the entire unit and both the external duties are affected by the substantial reflux ratio increase and need to be oversized.

Figure 7 shows similar trends for the Resilience Index RI as well. As expected, the resilience index exhibits a less conservative behaviour than the F_{SG} since it assesses the deviation of a single uncertain parameter at a time and both of them affect the unit flexibility in a comparable way. Thus, the curve profiles result more relaxed and the flexibility limit lies at about $RI = 11\,\%$. However, since the RI is a deterministic index as well, the changes in the curve slope are analogous to the F_{SG} index ones. A higher profitability of the indirect configuration with respect to the DWC is obtained for $RI \leq 4.5\,\%$ and after $RI = 9\%$ the operation with the intensified configuration becomes practically unfeasible.

As a main conclusion to be drawn from this economic assessment, it can be pointed out that, although more profitable under nominal operating conditions, process intensified design solutions suffer from a higher sensitivity with respect external deviations. As a consequence, for a given design they exhibit lower flexibility or, inversely, for a given flexibility requirement they need higher investments. In particular, if external disturbances are likely to occur, a preliminary flexibility assessment is of critical importance to understand which is the optimal layout and unit design and to have a reliable quantification of their real costs and benefits.

The same remarks related to the optimal design configuration apply as well when selecting the optimal number of equilibrium stages. In particular, a higher number of stages could not be the optimal solution under nominal operating conditions but could considerably help to mitigate the reflux ratio increase in case of high magnitude perturbations.

The observations related to the economic aspects are extended to the sustainability ones accounting for the process Global Warming Potential (GWP) indicator in the following section.

4.2 Environmental Assessment

The Global Warming Potential under perturbated operating conditions has been assessed for the indirect distillation train configuration as well as for the three

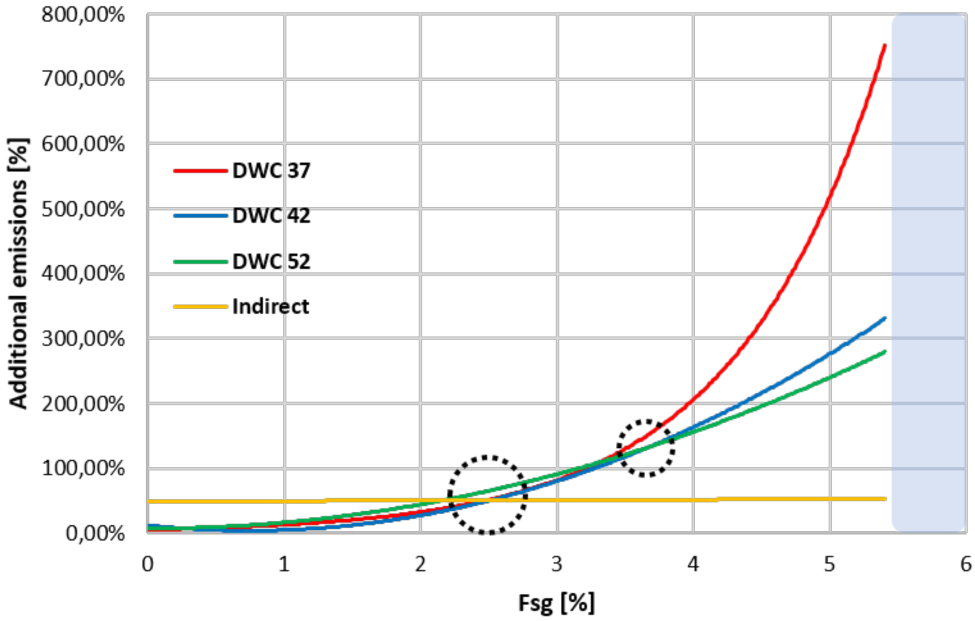


Fig. 8: GWP vs F_{SG}

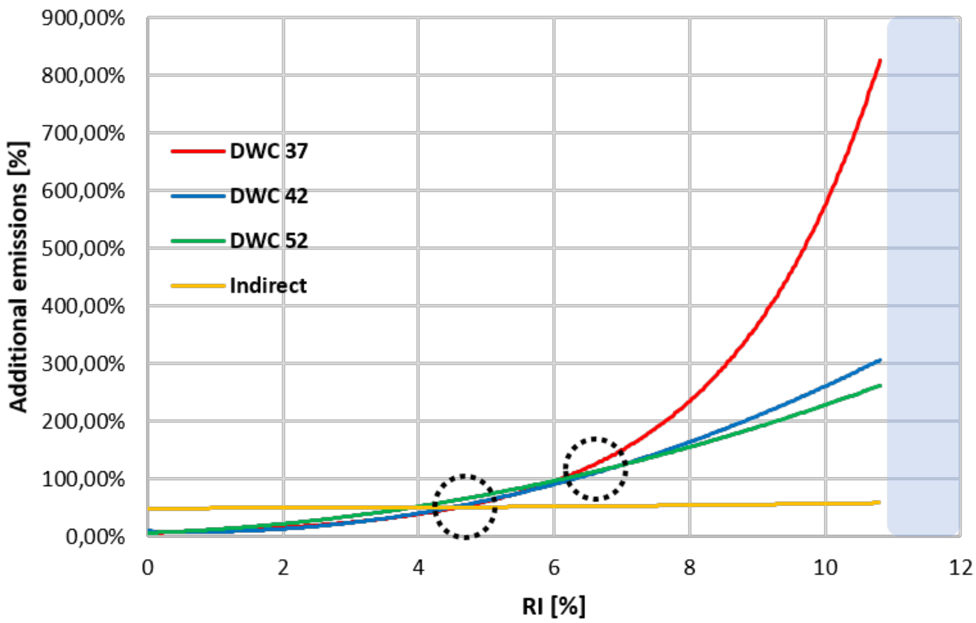


Fig. 9: GWP vs RI

Dividing Wall Column design layouts. Further details about the employed correlations can be found in Appendix D.

As discussed by several authors [42, 43, 44, 45], over the entire plant life, the CO_2 emissions related to the equipment can be neglected with respect to those considerably higher related to the energy consumption. In particular, for distillation columns, the reboiler heat duty plays the main role from a GWP perspective followed by the emissions related to the electricity consumption required for pumping.

If we look at the corresponding Figures 8 & 9 indeed they reflect the trend of OPerating Expenses and the additional costs in general. The DWC with respect to the indirect distillation train shows about 30 % lower emissions under nominal operating conditions. However, as for the economic assessment, higher reflux ratio and then external duties are required in case of external perturbations to be accommodated. In the DWC configuration, since only two duties can be managed, the energy demand for the process integrated solution increases much faster than for the distillation train where the majority of the perturbation is mitigated in the first column that purifies the most abundant component (i.e. butanol). From this result, it can be deducted that, when managing the process duties to deal with external disturbances, intensified equipment does not allow for the delocalization of the perturbation impact.

In Figure 8, the three curves for a DWC with 37, 42 and 52 equilibrium stages respectively are compared according to the F_{SG} Swaney & Grossman flexibility index. Under nominal operating conditions and until $F_{SG} = 3.6\,\%$ the configuration with 42 stages results to be the one with the lower emissions. In particular, the difference between the 37 and 42 stages curves start from a negligible value under nominal operating conditions and becomes higher and higher as flexibility increases since the lower number of stages implies a faster increase in the reflux ratio with respect to the other configurations. The same behaviour can be detected for the 42 stages configuration as well; when flexibility approaches $F_{SG} = 3.6\,\%$ indeed the 52 stages DWC is still able to mitigate the perturbation, and thus the reflux ratio, while the 42 stages column goes closer to the exponential growth of the reflux ratio as for the economic assessment. It can be then remarked that, for a given TAC (or even lower in case of 42 vs 37 stages), higher investments result in a lower impact of external perturbations from an energy efficiency point of view.

On the other hand, as for the economic assessment, there is a breakeven point between the DWC and the indirect distillation train emissions at about $F_{SG} = 2.4\,\%$ that makes the intensified configuration less sustainable than the conventional one. This gap becomes particularly significant for a flexibility higher than $F_{SG} = 4\,\%$ where the DWC becomes extremely unsustainable from a GWP perspective.

Analogous remarks apply to the Resilience Index as well. In particular, for a resilience index RI value of about 4% the additional emissions curve of the DWC overcomes the indirect configuration one whose slope is considerably lower. Moreover, after the 9.2% flexibility, where the additional equivalent CO_2 emissions are already two times higher, the slope of the DWC trend, drastically increases making the operation practically impossible to afford from an environmental point of view.

If we compare the three DWC configurations, the Resilience Index value after which the higher number of equilibrium stages brings benefits from a sustainability perspective shifts to about 7 % due to the less conservative nature of this index with respect to the F_{SG} one. This behaviour shows that both deviations have comparable implications from a flexibility perspective.

It can then be stated that the environmental assessment provides the decision maker a useful tool to evaluate the process design solution with the lower GWP over the entire feasible domain for different flexibility requirements. In particular, the distillation train exhibits worse performances under nominal operation with respect to process integrated design choices, such as DWC, but it show a less sensitive response when operating conditions are likely to undergo external perturbations.

In the range of DWC different layouts, the best number of stages from a sustainability perspective depends on the expected perturbation magnitude. To be more precise, columns with a higher number of stages are able, as expected, to mitigate the system response thanks to the capacity of better distributing the disturbance along the column trays.

5 Conclusions

The main goal of this paper is to analyze and discuss the criticalities associated to process integration when operating conditions uncertainty should be accounted for. These implications have been assessed both from an economic and an environmental perspective.

For this purpose, an ABE/W mixture separation case study has been considered since its upstream processing is likely to exhibit deviations in terms of product concentrations and its separation is characterized by feasibility constraints.

The DWC optimal design under nominal operating conditions showed investment costs about the 30% lower with respect to the distillation train and an analogous trend can be found for the equivalent CO_2 emissions. However, when external disturbances are included the integrated design solution requires a more considerable oversizing than the conventional configuration due to the lower number of duties and reflux streams that can be independently managed. In fact, the usual exponential trend exhibited by the TAC in proximity of the feasibility boundaries resulted to be emphasized by an order of magnitude because of the process integration. This behaviour causes the DWC column to progressively lose its higher profitability with respect to the series of standard distillation columns until it becomes even more expensive than the equivalent distillation train and, after a limit flexibility value, practically unaffordable.

The optimal number of stages for the integrated solution was discussed as well. On the one hand, for low flexibility values, the optimal design configuration still remains the most profitable one. On the other hand, whether the perturbation intensity to be withstood becomes considerably higher, a higher derivative is obtained for the additional costs vs. flexibility curve. In those cases, increasing the number of equilibrium stages with respect to the nominal value would be of critical importance for the column in order to mitigate the external disturbances without the need of an excessive reflux ratio and then external duty requirement resulting in bigger equipment as well.

As concerns the comparison between the two different flexibility index, the results proved that both water and n-butanol content have a considerable and comparable impact on the process flexibility due to their substantially different value.

From the environmental point of view a similar trend can be outlined. Under nominal operating conditions the DWC unit allows to reduce the CO_2 emissions by 33 %. The GWP resulted mainly affected by the reboiler heat duty and the electricity for pumping (5%) and for this reason reflects the operating costs related to a higher reflux ratio when deviations occur. Even in this case there exists a flexibility value after which process integration is not a more sustainable solution anymore. More in general, it can be stated that, when flexibility requirements become relevant, the environmental performance of the system can be compromised by process integration.

The same remarks about the DWC number of stages apply from the sustainability perspective as well. While for low flexibility values there are no considerable advantages in the addition of equilibrium stages from an environmental perspective, for substantially higher deviation magnitude indeed more equilibrium stages can ensure a lower energy requirement and thus lower CO_2 emissions reinforcing the results already obtained during the economic assessment.

For the specific case study, it can be concluded that the analysis revealed not only that the optimal configuration (indirect vs. DWC) under nominal operating conditions could underperform in case of external perturbations but also that, for a given configuration, the number of stages allowing for a profitable operation could vary according to the expected deviation magnitude.

To be more precise, this study highlights that, even though process integration is considered the best practice, its limitations should be quantified by means of a preliminary flexibility assessment that is strictly required when operating conditions are likely to undergo external disturbances. This procedure allows to accurately assess the "optimality" of the employed design solution for each deviation range.

From a more general perspective, a correlation between process integration, flexibility, costs and emissions can be deducted. More flexibile units require indeed higher investments that, if not taken into account during the design phase, could results in higher operating costs when dealing with process perturbation. The increasing energy duty demand is then reflected into more considerable emissions. In this context, process intensified equipment, although particularly effective when optimized for a given operating condition, amplifies the effect of all these implications by orders of magnitude in case of external perturbations.

A List of acronyms and symbols

Symbol	Definition	Unit
A	Characteristic dimension	m^n
ABE/W	Acetone-Butanol-Ethanol/Water	1
$C\%$	Carbon content percentage	%
C_{ij}^n	Excess Gibbs energy coefficients	$J/(mol \cdot K^n)$
C_{BM}	Equipment bare module cost	\$
C_p^0	Purchase equipment cost in base conditions	\$
$CAPEX$	CAPital EXpenses	$\$/y$
DWC	Divided Wall Column	acronym
d	Design variables	variable
F_{BM}	Bare module factor	1
F_M	Material factor	1
F_P	Pressure factor	1
F_q	Column trays factor	1
F_{SG}	Swaney and Grossman Index	1
f_j	Feasibility constraint	function
g_{ij}	NRTL excess Gibbs energy	J/mol
GWP	Global Warming Potential	$kgCO_2 - eq$
h_{steam}	Steam enthalpy	kJ/kg
$HPAD$	Heat pump assisted distillation	acronym
LLE	Liquid-Liquid equilibrium	acronym
$M\&S$	Marshall & Swift cost index	1
$MILNP$	Mixed Integer Non Linear Programming	acronym
N	Number of equilibrium stages	1
NHV	Net Heating Value	kJ/kg
$NRTL$	Non-Random Two Liquid model	acronym
$OPEX$	OPerating EXpenses	$\$/y$
P	Pressure	bar
Q	Heat duty	kJ/h
Q_{reb}	Reboiler heat duty	kJ/h
Q_{fuel}	Fuel heat duty	kJ/h
R	Ideal gas constant	$J/K/mol$

RI	Resilience Index	1
T	Temperature	K
TAC	Total Annualized Cost	$\$/y$
VLE	Vapor-Liquid equilibrium	acronym
z	Control variables	variable

Greek letters	**Definition**	**Unit**
α	$CO_2 - to - C$ molar mass ratio	1
α_{ij}	Non-randomness parameter	1
γ_i	Activity coefficient	1
δ	Flexibility index scale factor	1
Δ	Deviation	1
$\Theta(\delta)$	Flexibility hyperrectangle	1
θ_i	Uncertain parameter	variable
λ_{steam}	Steam latent heat	kJ/kg
τ_{ij}	NRTL dimensionless interaction parameter	1

B Thermodynamic model

As already anticipated, several authors [7, 24, 28, 30, 31, 32] state that the Non-Random Two Liquids (NRTL) [46] is the most suitable activity model to describe the ABE/W mixture behaviour. It is able to describe both liquid and vapor phases non-idealities such as azeotropes and liquid immiscibility.

The activity coefficient for the species i in a mixture of n components is given by:

$$ln(\gamma_i) = \frac{\sum_{j=1}^{n} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{n} x_k \cdot G_{ki}} + \sum_{j=1}^{n} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \cdot \left(\tau_{ij} - \frac{\sum_{m=1}^{n} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{n} x_k \cdot G_{kj}} \right) \tag{B.1}$$

where:

$$ln(G_{ij}) = -\alpha_{ij} \cdot \tau_{ij} \tag{B.2}$$

$$\alpha_{ij} = \alpha_{ij}^0 + \alpha_{ij}^1 \cdot T \tag{B.3}$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{R \cdot T} \tag{B.4}$$

$$\Delta g_{ij} = g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^1 \cdot T \tag{B.5}$$

where α_{ij} is called non-randomness parameter and τ_{ij} is called dimensionless interaction parameter.

Binary interaction parameters provided by process simulators are not compliant with each other and they're not always able to correctly predict the equilibrium compositions in proximity of the singularity points. Simulis® Thermodynamics database resulted the most reliable for water-alcohols interactions but some parameters for binary interaction coefficients among inorganic compounds are not available and needed to be adjusted in order to meet the experimental data.

C Capital costs estimations

In order to evaluate the investment required to build up a process plant or for whatever economic analysis and comparison related to process equipment, the cost of every single unit needs to be estimated.

For this purpose the Guthrie-Ulrich-Navarrete correlations described in the following paragraphs have been employed [38, 39, 40, 41].

C.1 Purchase equipment cost in base conditions

The purchase equipment cost in base conditions is obtained by means of the following equation:

$$log_{10}(C_P^0[\$]) = K_1 + K_2 \cdot log_{10}(A) + K_3 \cdot [log_{10}(A)]^2 \tag{C.1}$$

where A is the unit characteristic dimension and the K_i coefficients are relative to the equipment typology (cf. Table 3).

Equipment	**Typology**	K_1	K_2	K_3	**A**
Heat exchanger	Fixed tubes	4.3247	-0.3030	0.1634	Heat tranfer area $[m^2]$
	Kettle	4.4646	-0.5277	0.3955	Heat transfer area $[m^2]$
Columns (vessel)	Packed/tray	3.4974	0.4485	0.1074	Volume $[m^3]$
Trays	Sieved	2.9949	0.4465	0.3961	Cross sectional area $[m^2]$

Tab. 3: Equipment cost in base conditions parameters

Equipment	**Typology**	B_1	B_2	F_M	F_P
Heat exchanger	Fixed tubes	1.63	1.66	1	1
	Kettle	1.63	1.66	1	$F_{P,Kettle}$
Columns/vessel	/	2.25	1.82	1	1
Pumps	Centrifugal	1.89	1.35	1.5	1

Tab. 4: Bare module parameters

The provided coefficients refer to a Marshall & Swift equipment cost index equal to 1110. In order to update the cost estimations, a M&S index equal to 1638.2 will be used in order to refer the calculations to the year 2018 by means of the correlation:

$$C^0_{P,2} = \frac{M\&S_2}{M\&S_1} \cdot C^0_{P,1} \tag{C.2}$$

C.2 Bare module cost

The equipment bare module cost can be calculated according to the following correlation:

$$C_{BM} = C^0_P \cdot F_{BM} \tag{C.3}$$

where the bare module factor is given by:

$$F_{BM} = B_1 + B_2 \cdot F_M \cdot F_P \tag{C.4}$$

The F_M and F_P factors refers to the actual constructions materials and operating pressure while the B_i coefficients refers to the equipment typology (cf. Table 4).

The $F_{P,Kettle}$ value is given by:

$$log_{10}(F_P) = 0.03881 - 0.11272 \cdot log_{10}(P) + 0.08183 \cdot [log_{10}(P)]^2 \tag{C.5}$$

where P is the relative pressure in *bar*.

For column trays bare module cost a slightly different correlation should be used:

$$C_{BM} = N \cdot C_P^0 \cdot F'_{BM} \cdot F_q \tag{C.6}$$

where N is the real trays number, $F_{BM} = 1$ e F_q is given by:

$$\begin{cases} log_{10}(F_q) = 0.4771 + 0.08561 \cdot log_{10}(N) - 0.3473 \cdot [log_{10}(N)]^2 & if\ N < 20 \\ F_q = 1 & if\ N \geq 20 \end{cases} \tag{C.7}$$

D Global Warming Potential calculations

The indicator associated to the greenhouse effect impact category is the Global Warming Potential whose unit is $kg\,CO_2 - eq$ per unit.

$$CO_2 = \left(\frac{Q_{fuel}}{NHV}\right) \cdot \left(\frac{C\%}{100}\right) \cdot \alpha \tag{D.1}$$

where:

- CO_2 is the value of equivalent carbon dioxide emission in $[kg/h]$;
- NHV is the Net Heating Value and it is equal to 51,600 kJ/kg for Natural Gas;
- $C\%$ is the carbon content in percentage and it is equal to 75.4 for Natural Gas;
- α is the CO_2-to-C molar mass ratio and it is equal to 3.67.

Finally the term Q_{fuel} identifying the combustion energy required to vaporize the desired amount of steam can be estimated as:

$$Q_{fuel} = \left(\frac{Q_{reb}}{\lambda_{steam}}\right) \cdot (h_{steam} - 419) \cdot \left(\frac{T_F - T_0}{T_F - T_S}\right) \tag{D.2}$$

where:

- Q_{reb} is the reboiler duty in kJ/h ;
- λ_{steam} is the steam latent heat in kJ/kg ;
- h_{steam} is the steam enthalpy in kJ/kg ;
- 419 is the water enthalpy at $100\,°C$ in kJ/kg;
- T_F is the flame temperature in K;
- T_S is the stack temperature in K ;
- T_0 is the standard temperature in K .

On the other hand, the equivalent carbon dioxide emissions for pumping were estimated by multiplying the power needed by each pump and the amount of CO_2 per each GJ of electrical energy [42].

References

[1] Reay, D., Ramshaw, C., Harvey, A., 2011. Process Intensification: Engineering for Efficiency, Sustainability and Flexibility. Butterworth-Heinemann

[2] Stankiewicz, A.I. and Moulijn, J.A. (2000) Process Intensification: Transforming Chemical Engineering. Chemical Engineering Progress, 96, 22-34.

[3] Díez, E., Langston, P., Ovejero, G., Romero, M.D., 2009. Economic feasibility of heat pumps in distillation to reduce energy use. Applied Thermal Engineering 29, 1216–1223. https://doi.org/10.1016/j.applthermaleng.2008.06.013

[4] Jana, A.K., 2014. Advances in heat pump assisted distillation column: A review. Energy Conversion and Management 77, 287–297. https://doi.org/10.1016/j.enconman.2013.09.055

[5] Schultz, M.A., Stewart, D.G., Harris, J.M., Rosenblum, S.P., Shakur, M.S., O'Brien, D.E., 2002. Reduce costs with dividing-wall columns. Chemical Engineering Progress 98, 64–71

[6] Petlyuk, F.B., 1965. Thermodynamically Optimal Method for Separating Multicomponent Mixtures. Int. Chem. Eng. 5, 555–561

[7] Kiss, A.A., 2013. Advanced Distillation Technologies: Design, Control and Applications, 1 edition. ed. Wiley, Chichester, West Sussex, United Kingdom

[8] Glinos, K., Malone, M.F., 1988. Optimality regions for complex column alternatives in distillation systems. Chemical Engineering Research and Design 66, 229–240

[9] Becker, H., Godorr, S., Kreis, H., Vaughan, J., 2001. Partitioned Distillation Columns -- Why, When & How. Chemical Engineering 108, 68–68

[10] Petlyuk, F.B., 2004. Distillation Theory and its Application to Optimal Design of Separation Units. Cambridge University Press

[11] Triantafyllou, C., Smith, R., 1992. The design and optimisation of fully thermally coupled distillation columns : Process design. Chem. eng. res. des 70, 118–132

[12] Muralikrishna, V., Madhavan, K.P., Shah, S.S., 2002. Development of dividing wall distillation column design space for a specified separation. https://doi.org/10.1205/026387602753501870

[13] Seihoub, F.-Z., Benyounes, H., Shen, W., Gerbaud, V., 2017. An Improved Shortcut Design Method of Divided Wall Columns Exemplified by a Liquefied Petroleum Gas Process. Ind. Eng. Chem. Res. 56, 9710–9720. https://doi.org/10.1021/acs.iecr.7b02125

[14] Dünnebier, G., Pantelides, C.C., 1999. Optimal Design of Thermally Coupled Distillation Columns. Ind. Eng. Chem. Res. 38, 162–176. https://doi.org/10.1021/ie9802919

[15] Amminudin, K.A., Smith, R., 2001. Design and Optimization of Fully Thermally Coupled Distillation Columns: Part 2: Application of Dividing Wall Columns in Retrofit. Chemical Engineering Research and Design, Distillation and Absorption 79, 716–724. https://doi.org/10.1205/026387601753192037

[16] Hoffmann, A., Bortz, M., Burger, J., Hasse, H., Küfer, K.-H., 2016. A new scheme for process simulation by optimization: distillation as an example, in: Kravanja, Z., Bogataj, M. (Eds.), Computer Aided Chemical Engineering, 26 European Symposium on Computer Aided Process Engineering. Elsevier, pp. 205–210. https://doi.org/10.1016/B978-0-444-63428-3.50039-4

[17] Waltermann, T., Sibbing, S., Skiborowski, M., 2019. Optimization-based design of dividing wall columns with extended and multiple dividing walls for three- and four-product separations. Chemical Engineering and Processing - Process Intensification 146, 107688. https://doi.org/10.1016/j.cep.2019.107688

[18] Hoch, P.M., Eliceche, A.M., 1996. Flexibility analysis leads to a sizing strategy in distillation columns. Comput. Chem. Eng. 20, S139–S144. https://doi.org/10.1016/0098-1354(96)00034-8

[19] Swaney, R.E., Grossmann, I.E., 1985. An index for operational flexibility in chemical process design. Part I: Formulation and theory. AIChE J. 31, 621–630. https://doi.org/10.1002/aic.690310412

[20] Saboo, A.K., Morari, M., Woodcock, D., 1985. Design of Resilient Processing Plants .8. a Resilience Index for Heat-Exchanger Networks. Chem. Eng. Sci. 40, 1553–1565. https://doi.org/10.1016/0009-2509(85)80097-X

[21] Pistikopoulos, E.N., Mazzuchi, T.A., 1990. A Novel Flexibility Analysis Approach for Processes with Stochastic Parameters. Comput. Chem. Eng. 14, 991–1000. https://doi.org/10.1016/0098-1354(90)87055-T

[22] Lai, S.M., Hui, C.-W., 2008. Process Flexibility for Multivariable Systems. Ind. Eng. Chem. Res. 47, 4170–4183. https://doi.org/10.1021/ie070183z

[23] Di Pretoro, A., Montastruc, L., Manenti, F., Joulia, X., 2019. Flexibility analysis of a distillation column: Indexes comparison and economic assessment. Comput. Chem. Eng. 124, 93–108. https://doi.org/10.1016/j.compchemeng.2019.02.004

[24] Di Pretoro, A., Montastruc, L., Manenti, F., Joulia, X., 2020. Flexibility assessment of a biorefinery distillation train: Optimal design under uncertain conditions. Computers & Chemical Engineering 138, 106831. https://doi.org/10.1016/j.compchemeng.2020.106831

[25] IEA Bioenergy Annual Report 2018 retrieved at https://www.ieabioenergy.com/wp-content/uploads/2019/04/IEA-Bioenergy-Annual-Report-2018.pdf

[26] García, V., Päkkilä, J., Ojamo, H., Muurinen, E., Keiski, R.L., 2011. Challenges in biobutanol production: How to improve the efficiency? Renew. Sustain. Energy Rev. 15, 964–980. https://doi.org/10.1016/j.rser.2010.11.008

[27] Xue, C., Zhao, J.-B., Chen, L.-J., Bai, F.-W., Yang, S.-T., Sun, J.-X., 2014. Integrated butanol recovery for an advanced biofuel: current state and prospects. Appl Microbiol Biotechnol 98, 3463–3474. https://doi.org/10.1007/s00253-014-5561-6

[28] Errico, M., Sanchez-Ramirez, E., Quiroz-Ramìrez, J.J., Rong, B.-G., Segovia-Hernandez, J.G., 2017. Multiobjective Optimal Acetone–Butanol–Ethanol Separation Systems Using Liquid–Liquid Extraction-Assisted Divided Wall Columns. Ind. Eng. Chem. Res. 56, 11575–11583. https://doi.org/10.1021/acs.iecr.7b03078

[29] Di Pretoro, A., Ciranna, F., Fedeli, M., Joulia, X., Montastruc, L., Manenti, F., 2021. A Feasible Path-Based Approach for an Optimal Dividing Wall Column Design Procedure. Computers & Chemical Engineering, 149, 107309.

[30] Di Pretoro, A., Montastruc, L., Manenti, F., Joulia, X., 2020. Exploiting Residue Curve Maps to Assess Thermodynamic Feasibility Boundaries under Uncertain Operating Conditions. Ind. Eng. Chem. Res. 59, 16004–16016. https://doi.org/10.1021/acs.iecr.0c02383

[31] Patraşcu, I., Bîldea, C.S., Kiss, A.A., 2017. Eco-efficient butanol separation in the ABE fermentation process. Separation and Purification Technology 177, 49–61. https://doi.org/10.1016/j.seppur.2016.12.008

[32] Okoli, C. O.; Adams, T. A., II Design of dividing wall columns for butanol recovery in a thermochemical biomass to butanol process. Chem. Eng. Process. 2015, 95, 302.

[33] Gómez-Castro, F.I., Rodríguez-Ángeles, M.A., Segovia-Hernández, J.G., Gutiérrez-Antonio, C., Briones-Ramírez, A., 2011. Optimal Designs of Multiple Dividing Wall Columns. Chemical Engineering & Technology 34, 2051–2058. https://doi.org/10.1002/ceat.201100176

[34] Vazquez–Castillo, J.A., Venegas–Sánchez, J.A., Segovia–Hernández, J.G., Hernández-Escoto, H., Hernández, S., Gutiérrez–Antonio, C., Briones–Ramírez, A., 2009. Design and optimization, using genetic algorithms, of intensified distillation systems for a class of quaternary mixtures. Computers & Chemical Engineering 33, 1841–1850. https://doi.org/10.1016/j.compchemeng.2009.04.011

[35] Ge, X., Yuan, X., Ao, C., Yu, K.-K., 2014. Simulation based approach to optimal design of dividing wall column using random search method. Computers & Chemical Engineering 68, 38–46. https://doi.org/10.1016/j.compchemeng.2014.05.001

[36] Nguyen, T.D., Rouzineau, D., Meyer, M., Meyer, X., 2016. Design and simulation of divided wall column: Experimental validation and sensitivity

analysis. Chemical Engineering and Processing: Process Intensification 104, 94–111. https://doi.org/10.1016/j.cep.2016.02.012

[37] Ramapriya, G.M., Tawarmalani, M., Agrawal, R., 2014. Thermal coupling links to liquid-only transfer streams: A path for new dividing wall columns. AIChE Journal 60, 2949–2961. https://doi.org/10.1002/aic.14468

[38] Guthrie, K.M. , 1969. Capital cost estimating. Chem. Eng. 76 (3), 114–142 .

[39] Guthrie, K.M. , 1974. Process Plant Estimating, Evaluation, and Control. Craftsman Book Company of America .

[40] G. D. Ulrich, 1984, 'A Guide to Chemical Engineering Process Design and Economics', Wiley.

[41] P. F. Navarrete and W. C. Cole, 2001, 'Planning, Estimating, and Control of Chemical Construction Projects', 2nd Edition, CRC Press.

[42] Gadalla, M., Olujić, Ž., Jobson, M., Smith, R., 2006. Estimation and reduction of CO2 emissions from crude oil distillation units. Energy 31, 2398–2408.

[43] Yang, A., Sun, S., Eslamimanesh, A., Wei, S., Shen, W., 2019. Energy-saving investigation for diethyl carbonate synthesis through the reactive dividing wall column combining the vapor recompression heat pump or different pressure thermally coupled technique. Energy 172, 320–332. https://doi.org/10.1016/j.energy.2019.01.126

[44] Yang, A., Jin, S., Shen, W., Cui, P., Chien, I.-L., Ren, J., 2019. Investigation of energy-saving azeotropic dividing wall column to achieve cleaner production via heat exchanger network and heat pump technique. Journal of Cleaner Production 234, 410–422. https://doi.org/10.1016/j.jclepro.2019.06.224

[45] Tavan, Y., Shahhosseini, S., Hosseini, S.H., 2014. Design and simulation of ethane recovery process in an extractive dividing wall column. Journal of Cleaner Production 72, 222–229. https://doi.org/10.1016/j.jclepro.2014.03.015

[46] Renon H., Prausnitz J. M., 1968. "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", AIChE J., 14(1), S.135–144.