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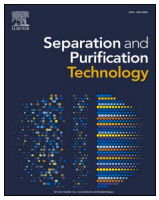

Thermally coupled distillation columns without vapor transfer – Current state and further needs

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ABSTRACT

Reducing the energy requirements is one essential pillar in the effort to reduce the carbon footprint of the energy intensive chemical industry. Thermal coupling of distillation columns and the equipment-integrated implementation in dividing wall columns can be considered a mature and established technology to reduce the energy demand of distillation sequences. Despite the widespread investigations and applications, the vaporous transfer stream between thermally linked columns or vapor split in the dividing wall column is associated with certain limitations. Some of these can effectively be overcome by adding an additional column section with reboiler or condenser to the thermally linked column, converting the bidirectional transfer of liquid and vapor to a unidirectional liquid transfer, which mandates additional investment, but provides an additional degree of freedom and retains the energy saving potential of the thermally coupled sequence. Although these so-called Liquid-Only-Transfer (LOT) sequences have been introduced almost 25 years ago, the process concept is receiving an increasing interest in recent years, with specific focus on conceptual design and control studies. The current review provides a methodological overview on synthesis, design and control studies for LOT-sequences, considering zeotropic and azeotropic distillation processes. It analyzes the advantages and challenges of this interesting process concept and highlights research areas and questions that still require additional attention.

Abbreviations: 3-DS, Three columns connected in direct sequence (uncoupled); 5-mDWC, Multiple dividing wall column with five product streams; 5-LOT-mDWC, Multiple dividing wall column with five product streams and LOT-streams; BTX, Benzene, toluene and xylene; CAPEX, Capital expenditure; CC, Composition control; CV, Control variable; DOF, Degree of freedom; DWC, Dividing wall column; DWC-SR, Dividing wall column with upper wall; DWC-SS, Dividing wall column with lower wall; DS, Direct sequence (uncoupled); E-DWC, Extractive dividing wall column; E-TC-SR, Extractive side rectifier; HETP, Height equivalent per theoretical stage; HI, Heat integration; HI-LOT-SR, Heat integrated LOT- side rectifier; IS, Indirect sequence (uncoupled); Kaibel-DWC, Dividing wall column with two side streams; LOT, Liquid-Only-Transfer; LOT-DWC, A dividing wall column with the wall extending through the column and LOT-streams; LOT-FC, Fully coupled LOT-sequence with two LOT-streams; LOT-FC-DWC, Dividing wall column with the wall extending through the column and LOT-streams in both rectifying and stripping section; LOT-Kaibel-FC, Kaibel-configuration with LOT-streams; LOT-mDWC, Multiple dividing wall column with LOT-streams; LOT-s-mDWC, Simplified multiple dividing wall column with LOT-streams; LOT-SR, LOT-side rectifier; LOT-SR-DWC, Dividing wall column with the wall extending through the column and LOT-stream in the stripping section; LOT-SS, LOT-side stripper; LOT^{UP}-TC^{LO}-DWC, Combined dividing wall column with LOT-stream in the rectifying section and thermal coupling/vapor split in the stripping section; LOT^{UP}-TC^{LO}-FC, Combined sequence with LOT-stream in the rectifying section and thermal coupling in the stripping section; mDWC, Multiple dividing wall column; MADS, Mesh Adaptive Direct Search; MESH, Mass balance, equilibrium relation, summation equation, energy balance; MINLP, Mixed integer nonlinear programming; MV, Manipulated variable; NLP, Nonlinear programming; NRTL, Nonrandom-two-liquid-model; NSGA, Non-dominated sorting genetic algorithm; OPEX, Operational costs; PF, Prefractionator sequence (uncoupled); PF^{UP}-LOT^{LO}, Combined sequence with prefractionator connection in the rectifying section and LOT-stream in the stripping section; PF^{UP}-TC^{LO}, Combined sequence with prefractionator connection in the rectifying section and thermal coupling in the stripping section; PF^{UP}-TC^{LO}-DWC, Combined dividing wall column with prefractionator connection in the rectifying section and thermal coupling/vapor split in the stripping section; RDWC, Reactive dividing wall column; R-LOT-SR, LOT-side rectifier with reactive zone; R-TC-SR, Side rectifier with reactive zone; SADDE, Self-adapting dynamic evolution algorithm; s-mDWC, Simplified multiple dividing wall column; TAC, Total annualized costs; TC, Thermal coupling/ thermally coupled; TC-FC, Fully thermally coupled sequence; TC-SR, Thermally coupled side rectifier; TC-SS, Thermally coupled side stripper; TC^{UP}-LOT^{LO}-FC, Combined sequence with thermal coupling in the rectifying section and LOT-stream in the stripping section; TC^{UP}-LOT^{LO}-DWC, Combined dividing wall column with thermal coupling/ liquid split in the rectifying section and LOT-stream in the stripping section; TC^{UP}-PF^{LO}, Combined sequence with thermal coupling in the rectifying section and prefractionator connection in the stripping section; TC^{UP}-PF^{LO}-DWC, Combined dividing wall column with thermal coupling/ liquid split in the rectifying section and prefractionator connection in the stripping section; TEMPC, Temperature control; VR, Vapor recompression; VR-LOT-DWC, Dividing wall column with LOT-streams and vapor recompression; VR-LOT-Kaibel-DWC, Kaibel dividing wall column with LOT-streams and vapor recompression.

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Nomenclature

α_i	Ratio of liquid side stream to internal liquid stream in the first column
β_i	Ratio of liquid side stream to internal liquid stream in the second column
Σ	Component matrix of singular value decomposition with singular values
σ	Singular value of Σ
A_i	Area of heat exchanger
d_i	Column diameter
D_i	Distillate stream
F_i	Feed stream
G	Sensitivity matrix
h_i	Column height
L_i	Side stream
N_i	Stage count
p_i	Pressure
Q_i	Heat duty
R_i	Reflux stream
RR_i	Reflux ratio
S_i	Side stream
T	Temperature
U	Component matrix of singular value decomposition with left singular vectors
V	Component matrix of singular value decomposition with right singular vectors
ΔV	Optimality region for a given separation
V_{min}	Minimum vapor flowrate for a given separation
x_i	Composition

1. Introduction

Distillation is one of the most important separation technologies in the chemical industry with more than 40 000 distillation columns in operation [1] which account for more than 90 % of all fluid separations [2]. Due to this widespread prevalence in combination with the generally high energy consumption of distillation columns, distillation is of substantial importance for the global industrial energy demand. Ambitious climate goals and steeply rising utility prices necessitate the research for process improvements and alternatives that are less energy demanding. Nevertheless, it is important to note that distillation is not per se an energy-inefficient separation technology [3] and that even under ideal assumptions other technologies do not easily outperform distillation on a general basis [4]. While distillation is rightfully considered as the most mature separation technology [5], considering the available know-how in equipment design and manufacturing, there are persistent misconceptions on the energy-efficiency [6], which mandate the need for more effective tools that cover the wealth of options to improve the energy-efficiency of distillation processes compared to simple non-integrated distillation columns, as e.g. illustrated in the study of Chavez Valesco et al. [7].

One effective and industrially established approach to reduce the energy consumption of distillation is heat and mass integration of multiple distillation columns within one sequence by replacing intermediate reboilers or condensers by a bi-directional vapor and liquid transfer, which is termed thermal coupling (TC). For a ternary separation in two columns, this commonly results in a thermally coupled side rectifier (TC–SR) (Fig. 1-(II)), a thermally coupled side stripper configuration (TC–SS) (Fig. 1-(V)) or a fully thermally coupled sequence (TC–FC) (Fig. 1-(VIII)), depending on the number and location of thermal couplings. Due to reduced mixing entropies at the feed locations the thermal coupling can offer significant energy saving potential and reduced equipment when compared to the uncoupled sequences [8]. However, it should be noted that the actual energy savings strongly depends on the specific mixture that is to be separated and the composition of the feed. For the TC-FC, which generally exhibits the lowest theoretical energy demand out of the three mentioned sequences [9], practical energy saving potentials of 30–40 % are reported [10,11]. As demonstrated by Halvorsen and Skogestad [12] the minimum vapor flowrate V_{min} of the fully thermally-coupled configuration for a three-product separation is the same as the more demanding separation between the light/intermediate and intermediate/high boiling product streams in a single column. The respective method of the V_{min}–diagrams allows for a convenient analysis of the minimum energy demand, even for multi-product separations [13]. In contrast, the second law thermodynamic efficiency of a sequence might decrease by using the TC-FC, since heat has to be provided at the highest temperature of the system (boiling temperature of high boiler) and is rejected at the lowest temperature of the system (boiling temperature of the light boiler) [14]. Although high heating utility temperatures are generally unfavorable for operational costs (OPEX), the TC-FC reportedly still exhibits significant saving potentials of around 20 % in steam costs [15]. Nevertheless, energy and cost savings need to be evaluated on a case-by-case basis, especially considering the recent and expected variations in energy prices.

In order to save not only on OPEX but also on capital expenditure (CAPEX), a further integration step is often conducted in practice, where the individual columns are integrated into a single column shell (Fig. 1-(III), (VI), (IX)). This is facilitated by introducing a physical wall in the column shell, which partitions the column and as such allows for the separation into more than two pure fractions in a single column shell. This equipment-integrated unit is termed dividing wall column (DWC) and is one of the most prominent examples of process intensification of separation processes [16].

DWCs combine the energy saving potential of thermally-coupled distillation processes with further investment savings of up to 30 % [17], construction space reductions by up to 40 % [15] and since multiple separations are conducted in a single process step, they are beneficial for the separation of temperature sensitive components [18]. Considering these significant CAPEX and OPEX savings, it is remarkable, that half a century lie between the first patent of a dividing wall column (Monro in 1935 [19] and Wright in 1946 [20]) and the first industrial implementation of a dividing wall column in 1985 at BASF [21]. One reason for this is the increased level of complexity of thermally coupled columns, calling for sophisticated design and control methods. While first contributions on this research topic were published in the 1970ies, especially around 2000 the number of publications started to steeply increase (Fig. 2), piling up to more than 1300 publications on thermally coupled distillation columns and DWCs to date. While most commercial process simulators still require manual construction of a respective surrogate model for a DWC [22], there are some exceptions [22] and several optimization-based design methods allow for the efficient design of three- and four-product DWCs for specific separation problems today [23–26]. Considering the apparent advancement of calculation methods and experimental analyses of process behavior in academic research and industry, it is not surprising that thermally coupled distillation columns and especially DWCs can be considered an industrially established process. While the exact number of industrial implementations of DWCs is hard to quantify, reported numbers list 36 implementations at BASF in 2004 [10] and around 50 applications at BASF and 100 applications worldwide in 2007 [27], as well as 70 applications at BASF in 2009 [17] and 300 applications worldwide in 2019 [28]. Dejanović [29] and Yildrim [30] provide extensive reviews on specific industrial implementation cases of DWCs, while dedicated reviews on process design

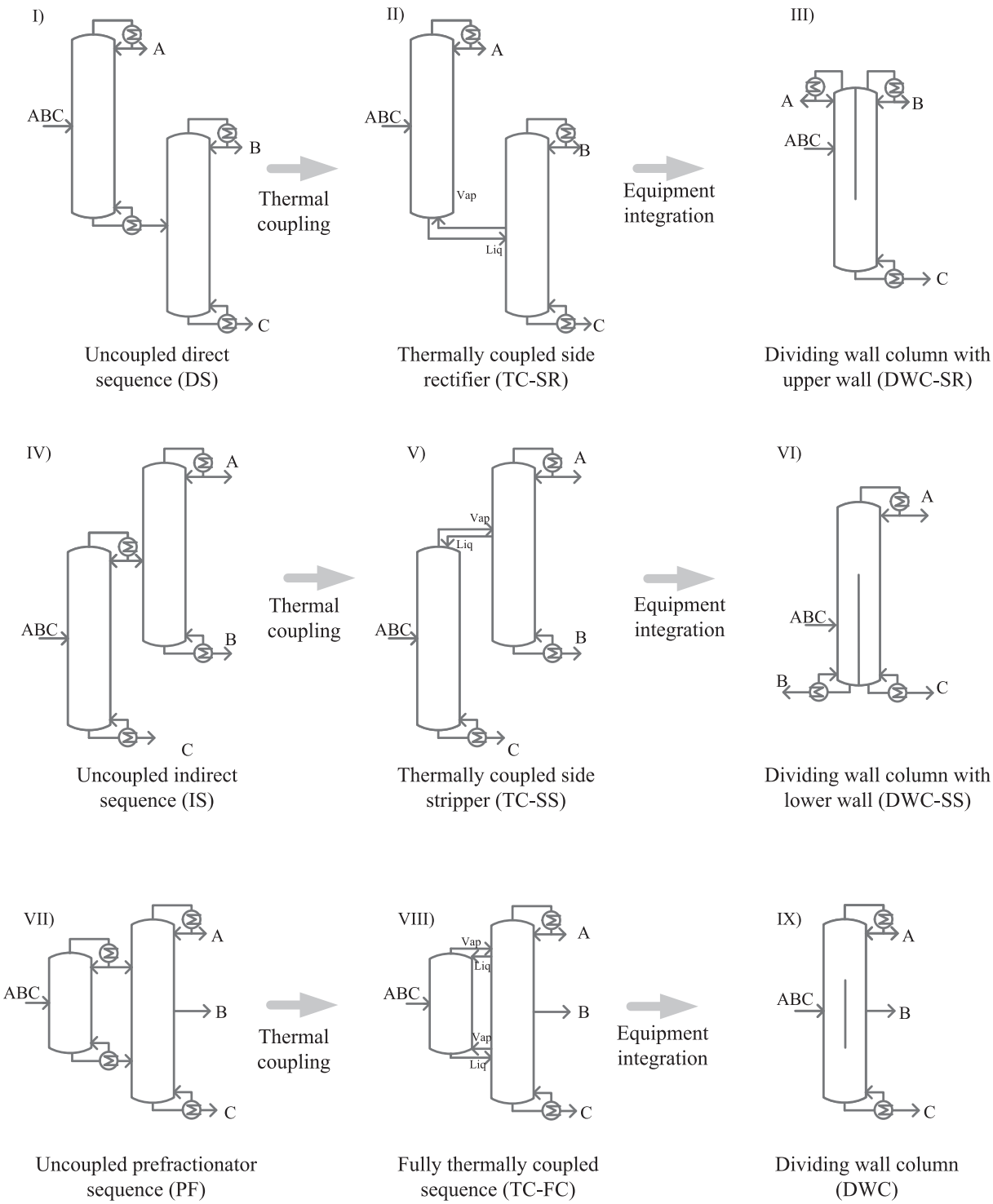

Fig. 1. Schematic of (I) an uncoupled direct distillation sequence (DS), (II) a thermally coupled side rectifier (TC-SR), (III) a dividing wall column with an upper dividing wall (DWC-SR), (IV) an uncoupled indirect distillation sequence (IS), (V) a thermally coupled side stripper (TC-SS), (IV) a dividing wall column with a lower dividing wall (DWC-SS), (VII) an uncoupled prefractionator sequence (PF), (VII) a fully coupled sequence (TC–FC) and (IX) a dividing wall column (DWC).

and optimization [24–26], process control [31], extractive DWCs [32] and reactive DWC [33] are available as well. There is certainly further room for improvement and further research, as e.g. most studies and implementations concern three-product separations, while the first industrial implementation of a four-product dual-dividing wall column was reported only last year [34]. However, overall research and expertise on DWC is obviously extensive.

While both research and implementations are impressive, it is important to note that there are also certain challenges in design and operation of DWC that do not only come along with an increased level of complexity, but also limit the range of applications of TC-Sequences and the respective DWC configurations.

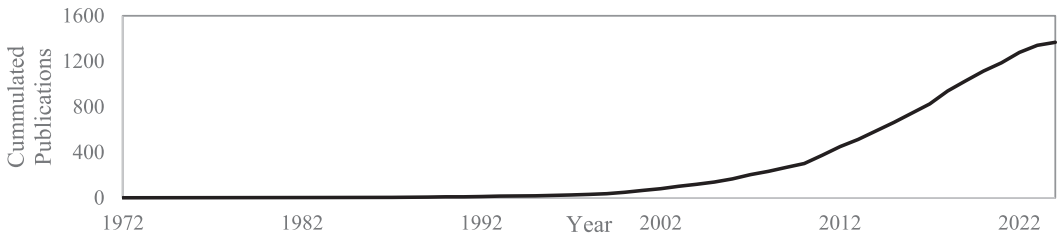

Fig. 2. Cumulated publications on thermally coupled distillation sequences (Scopus search for "Dividing wall column"/ "Divided wall column"/ "Thermally coupled side rectifier"/ "Thermally coupled side stripper"/ "Thermally coupled distillation").

1.1. Limitations of dividing wall columns and thermally coupled sequences

Since all of the separation steps are conducted in a single column shell for the DWC, there is only a single operating pressure (e.g. the top pressure) that has to be predetermined and is only affected by the pressure drop along the column height for all separation steps. According to Kaibel [10], who initiated the first industrial implementation of a DWC at BASF and significantly shaped industrial research in this topic, this aspect is one of the major limitations of DWCs. The operating pressure has a significant effect on the thermodynamic vapor–liquid equilibrium [35] and hydrodynamic effects [36] in a distillation column and is consequently one of the most essential degrees of freedom when designing a distillation process. Other than in a DWC, both columns in the DS, IS or PF-sequence can be operated at independent pressures, enabling a potentially favorable vapor–liquid equilibrium or a more favorable set of distillate or bottoms product temperatures. Furthermore, this variability in pressure and temperature settings may enable heat integration between the reboiler and condenser of the adjacent columns or with other heat sources and sinks in a heat exchanger network. Other than the DWC, TC-Sequences (TC-SR, TC-SS and TC-FC) still perform the separation steps in individual columns, such that there is some leeway as to setting individual pressures. However, there are still significant limitations due to the vaporous transfer streams and little research published on the individual pressure control of thermally coupled distillation columns.

For DWCs, the vapor split below the wall in the DWC-SR and between the prefractionator and the main column in the DWC is another bottleneck for the application, as it has a critical impact on the purities and the actual energy demand of the separation [37,38]. However, it is usually not a manipulated variable during operation [39]. Rather, the vapor split is self-adjusting based on the free cross section and pressure drop resulting from the column internals on both sides of the dividing wall or in the adjacent columns in the equivalent TC-FC configuration. This means, this value is fixed during the design stage and cannot be specifically regulated during operation. While there is some research on active vapor split control for DWCs [40–44], this concept has not found a widespread reported industrial application. In the TC-sequences the vapor stream can in principle be regulated via control valves, when the column that donates the vapor stream is at a higher pressure than the column that receives the vapor stream. Yet, this limits the flexibility in pressure design that uncoupled sequences present. Furthermore, while such a control valve-strategy can be realized in the TC-SR and TC-SS configurations practically, in the TC-FC configuration, this means the pressure profile has to be controlled meticulously due to the opposed directions of the vapor stream [45]. This could be circumvented by using compressors to transport the vapor from a lower-pressure column to a higher-pressure column, however it is generally not advised to implement compressors for this purpose due to their expensive acquisition and operation [46]. Furthermore, manipulating the vapor stream during operation might introduce additional issues like disrupting the pressure profile and influencing F-factors and as a consequence separation efficiency. In contrast, manipulating a liquid side stream via a pump or

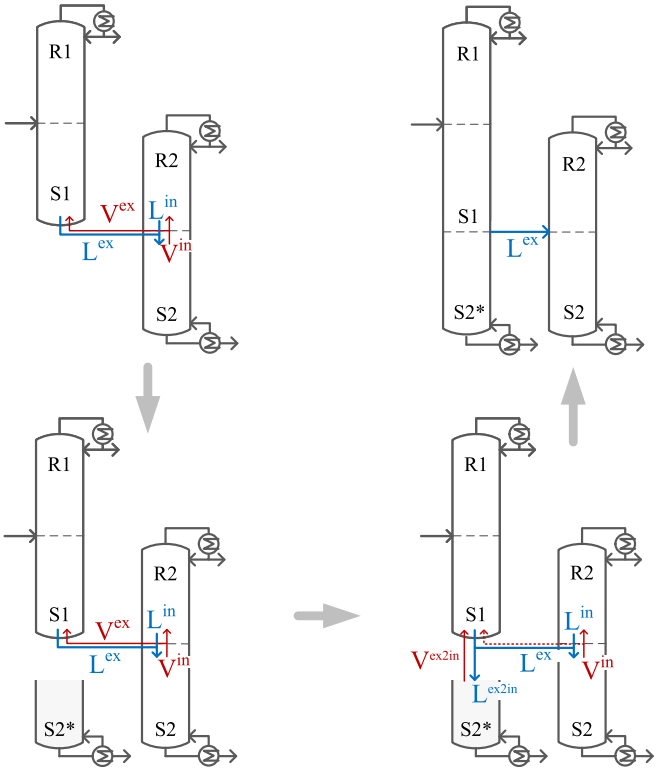

Fig. 3. Thermally coupled side rectifier (TC-SR) and thermodynamically equivalent liquid-only-transfer side rectifier (LOT-SR) based on Agrawal [50].

control valve does not influence the columns hydrodynamics to a similar extent, while only requiring a sufficient hold-up in the collector from which the side stream is withdrawn. This could potentially also be extended by means of an external vessel, similar to e.g. middle vessel batch distillation [47].

1.2. Liquid-Only-Transfer configurations

In order to overcome the limitations that originate from the bi-directional liquid and vapor transfer and vapor split in the DWC, Agrawal [48–50] proposed and patented a novel transformation of the thermally coupled process to the Liquid-Only-Transfer (LOT) configuration in 2000. The external vapor transfer/split is effectively eliminated by a systematic duplication and rearrangement of column segments as exemplarily depicted in Fig. 3 for the TC-SR configuration. In this implementation of TC-SR, the reboiler is located in the stripping section of the second column (S2). The vapor originating from this section is split into an internal vapor stream (V^{in}) transferred to the rectifying section of the second column (R2) and an external vapor stream (V^{ex}), which is transferred to the stripping section of the first column (S1). Column section S2 receives both an external as well as an internal liquid stream from both section R2 as well as S1 (L^{ex} and L^{in}, respectively) In

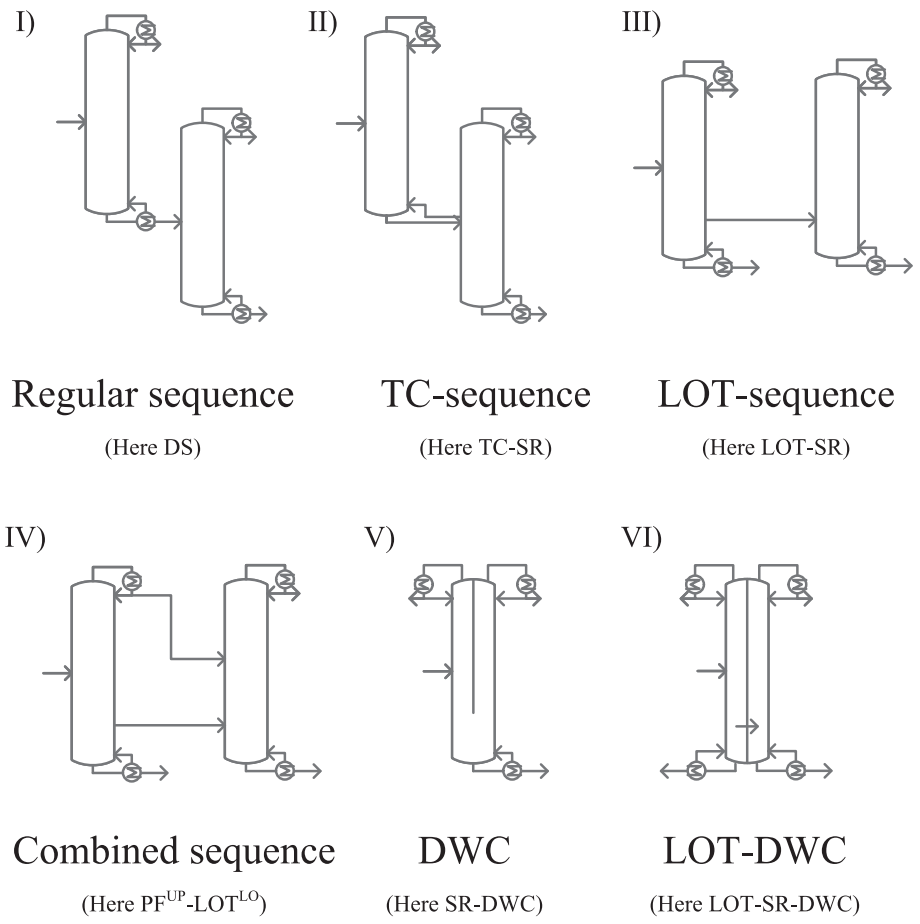

Fig. 4. Classification of configurations with I) regular sequences, II) TC- sequences, III) LOT–sequences, IV) combined sequences, V) DWCs and VI) LOT-DWCs.

the first step of the LOT-conversion, the stripping section and the connected reboiler of the second column (S2) is duplicated and introduced as extension (S2*) below the original stripping section S1 of the first column. The external vapor stream V^{ex} is now generated in the reboiler of the first column below S2*, further denoted as internal vapor stream within the first column (V^{ex2in}). Consequently, the two columns are exclusively connected via a liquid stream. A part of the previous external liquid stream is now processed as an internal liquid stream (L^{ex2in}) in the extended stripping section. Essentially, the net mass streams originally leaving and entering S2 are now divided up between S2 and S2*.

As initially described by Agrawal [50] and later proven by Ramapriya et al. [37] the theoretical minimal vapor flow, and the respective minimum energy requirement, of this LOT–sequence equals the minimum vapor flow of its conventional TC-counterpart. As such the LOT–sequences are considered thermodynamically equivalent to the TC-sequences and respective DWC configurations. While obtaining the same energy-saving potential at increased cost, due to requiring an additional column section and reboiler, might not seem attractive at first, there are some major benefits of the LOT–configuration resulting from the additional degrees of freedom. Overall, the LOT-sequences promise three main advantages over conventional TC-sequences and DWC, which have been at least theoretically analyzed and exploited to varying degrees in publications in recent years:

(I) Individual operating pressure for each column

Since the columns are only linked by a liquid stream, both columns can be operated at independent pressure. Thereby, thermal coupling can be considered for column sequences for which the boiling points of the individual products mandate different operating pressures, due to temperature sensitivity or utility limits. Modifying the pressure also enables further potential for heat integration by adjusting the temperature level at which heat is provided at the condenser or required at the reboiler, allowing for either direct heat integration between the columns or integration into a heat exchanger network of multiple process units. Finally, the influence of the operating pressure on the boiling temperature may also be exploited in integrated reactive distillations.

(II) Direct and indirect manipulation of all mass streams in the column

Other than the previously uncontrolled vapor splits, the liquid transfer streams can be effectively manipulated by a frequency-controlled pump, given a sufficient hold-up in the collector of the primary column. Each added heat exchanger further provides an additional manipulated variable that can be used to indirectly control the internal flows in the individual columns. This promises more flexibility and robust operation at the energy-optimal operating point.

(III) Possibility to retrofit existing column sequences

While the DWC provides a proven CAPEX saving potential for grassroot designs due to the equipment integration, a retrofit from a regular column to a DWC requires an increased separation effort in the column shell of the existing distillation column or an implementation of necessary extensions. The LOT-sequence may however enable a straightforward constructional retrofit from an existing uncoupled to a coupled LOT-sequence by utilizing both of the existing columns. As such, retrofitting to LOT-sequences offers OPEX savings with comparably low CAPEX and effort for modification.

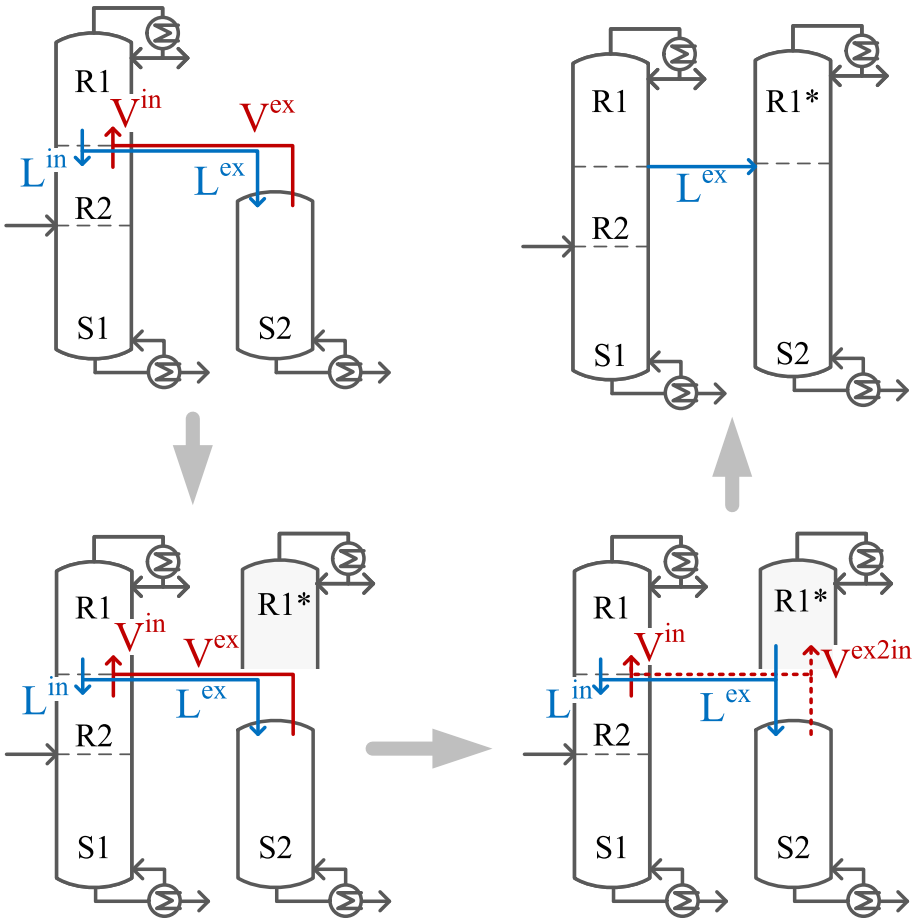

Fig. 5. Development of a thermally coupled side stripper TC-SS to a liquid-only-transfer side stripper LOT-SS based on Agrawal [50].

Despite these compelling arguments and potential for utilizing LOT-sequences, the concept has received limited attention compared with TC and DWC in the last 24 years since the initial proposal by Rakesh Agrawal [48–50]. The current contribution presents an exhaustive summary and review of the less than 100 publications concerning regular LOT-sequences and further integrated LOT-sequences, which cumulates to less than 10 % of the more than 1300 publications dedicated to thermal coupling and dividing wall columns. In this context, it should be noted, that since the concept is not as mature and well- known as e.g. DWC, no consistent terminology has been established. While we strongly promote the use of the original term introduced by Rakesh Agrawal [50] as "liquid-only-transfer", we encountered several other expressions, such as"liquid only side stream" [51,52], "side stream sequence" [53,54], "reduced vapor transfer" [55] and also "easy-to-operate" [56]. In the context of extractive distillation, it was e.g. introduced simply as "energy-efficient side-stream extractive distillation system" [57], despite recognizing the derivation from the LOT–concept of Agrawal. In this context it should be noted, that in 1986 Glinos et al. [58] introduced so-called "complex column arrangements", which consist of columns with side streams and multiple feeds. Although this de facto includes LOT-sequences, they are not considered as a derivation from thermally coupled sequences but rather as a combination of a side stream-column and a regular column. Hence, even though Glinos et al. [58] already mention the retrofitability of these complex column arrangements, the unique characteristics and advantages of LOT-sequences are not a focus of this contribution. Therefore, within this review article the publication of Agrawal [50] is regarded as the origin of the dedicated research on LOT.

While LOT–concepts have been investigated theoretically for a number of applications, ranging from zeotropic to azeotropic distillation and reactive distillation, to the best of our knowledge, not a single report on experimental validation or even industrial implementation of a dedicated LOT-sequences has been published so far. Yet, distillation columns with side streams and the interconnection of such a column with a subsequent regular column is certainly not a novum in industrial practice, such that configurations like LOT-sequences are likely employed and operated in industry, without specifically identifying them as LOT–configurations. Therefore, their benefits might not be utilized fully, such that systematic methods for the design and operation of LOT–sequences can provide further advantages. Therefore, the goal of this article is to provide a thorough overview and review of the state-of-the-art on research on LOT-sequences and evaluate open questions and research gaps towards a dedicated industrial implementation. In order to do so, we first provide an overview of the methods developed for synthesis, enumeration and shortcut evaluations (Section 2) and design (Section 3), prior to the operation and control of LOT-sequences for the separation of zeotropic mixtures (Section 4). Furthermore, the extended use of the LOT-concept to heat-integrated, as well as extractive and reactive distillation processes is investigated in Section 5. Finally, Section 6 concludes the evaluation and points at the respective research gaps that need to be addressed in the future to effectively exploit the analyzed potentials.

For the sake of an effective discussion in the manuscript, the different configurations are first classified according to their type of connection with the prefixes as illustrated in Fig. 4. "Regular sequences" are considered as thermally uncoupled columns. The direct sequence (DS) is used here for an exemplary illustration, while further examples are also illustrated in Fig. 1-(I), (IV) and (VII). "TC-sequences" are characterized as thermally coupled sequences with bidirectional vapor- and liquid links between the columns, here shown as the TC-SR. Further examples

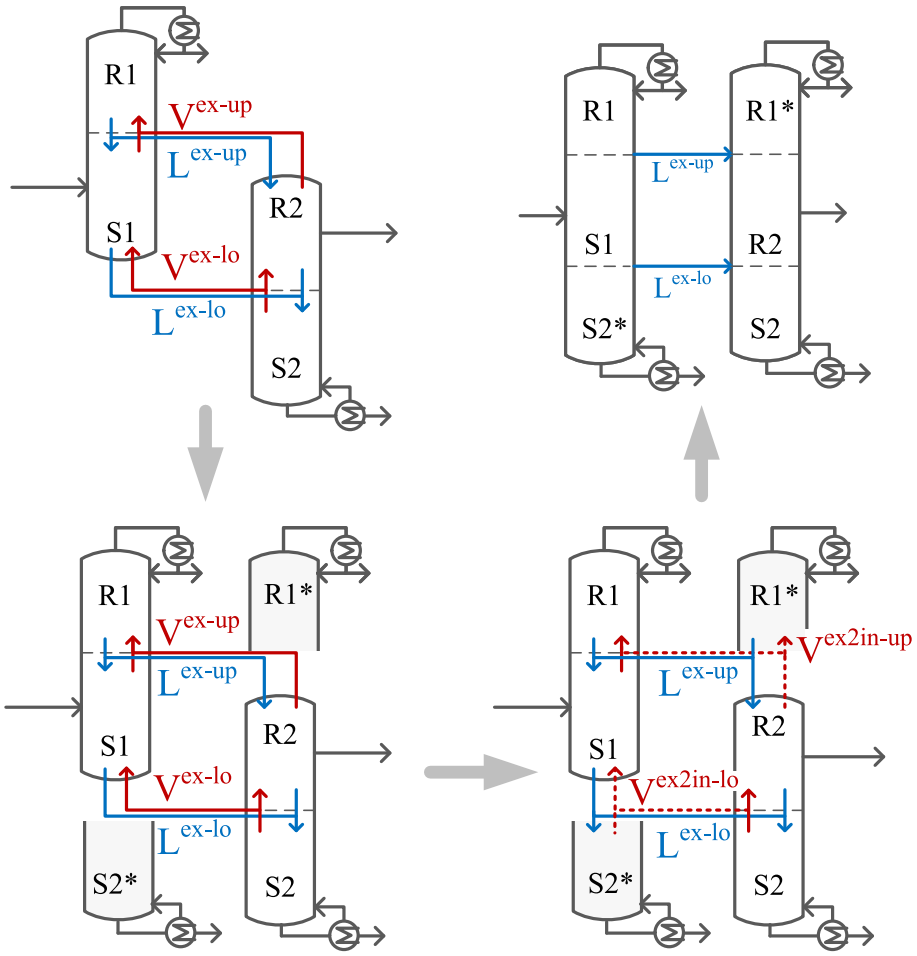

Fig. 6. Development of a fully coupled sequence TC-FC to a liquid–only–transfer fully coupled sequence LOT-FC based on Agrawal [50].

also given in Fig. 1-(II), (V) and (VIII). "LOT-sequences" are thermally coupled sequences characterized by one or more liquid side streams, here exemplary shown as the LOT–SR. Sequences that display more than one connection type are denoted as combined sequences in this contribution, shown here is the example PF^{UP}-LOT^{LO}. For these combined sequences, the connection type is supplemented with the location of this connection in subscript. A positioning in the rectifying section or the distillate of the first column is denoted as *UP* and a positioning in the stripping section or bottom stream of the first column as *LO*. "DWCs" (Further examples also given in Fig. 1-(III), (VI) and (IX)) are delimited from "LOT-DWCs", for which the dividing wall is extended, such that it partitions the whole column. The example shown in Fig. 4 is the LOT-SR-DWC, when there is a second LOT–stream in the upper part, the column is denoted as LOT-FC-DWC* (Shown in Figure SI–1 in the Supplementary Information). Many of these sequences are conceptually equivalent but structurally different, e.g. the LOT-SR and the LOT-SR-DWC. In many publications, these thermally coupled and DWC versions are treated as interchangeable. While this is viable for a thermodynamically-based investigation, of e.g. the minimum energy demand, it is not viable for the analysis of the fluid dynamics or equipment sizing and estimation of investment costs. E.g. the LOT-SR requires two columns whereas the LOT-SR–DWC requires only one column shell, but a more sophisticated set of internals. Due to the vast variety of sequences discussed in this contribution that fall into one of these categories, it is not expedient to sketch all of the sequences in the main text. Illustrations of all sequences marked with * are provided in Figure SI-1 to Figure SI-7 in the Supplementary Information.

2. Sequence Synthesis, enumeration and shortcut calculations

The basic procedure for developing LOT-sequences from TC-sequences has been illustrated in Section 1 for the LOT-SR. In his initial publication on the LOT-concept, Agrawal [50] demonstrated the concept for the basic LOT-SR, LOT-SS and LOT-FC. Furthermore, combined TC-LOT-sequences based on the TC-FC-sequence were shown as variations of the LOT-FC with two liquid streams and the LOT-concept is demonstrated for four-product separations in three columns as well. In this section, the synthesis of LOT-connections is further elucidated for both stripping as well as rectifying sections (Section 2.1). Subsequently, contributions based on the enumeration of up to quinary separations are discussed (Section 2.2). Furthermore, there are publication on shortcut calculations for LOT-sequences, which are reviewed in Section 2.3.

2.1. Synthesis

In order to demonstrate, how the duplication and stream rearrangement for a rectifying section works, the development of an LOT-SS based on an TC-SS is shown in Fig. 5. In the TC-SS, both columns are equipped with reboilers, whereas only the first column is equipped with a condenser. The vapor leaving the top of the stripping column (S2) is transferred to the first column (V^{ex}). The liquid stream stemming from the upper rectifying section of the first column (R1) is split into an internal liquid stream (L^{in}) entering the lower rectifying sections of the first column (R2) and an external liquid stream (L^{ex}). In order to create the LOT-sequence, the section R1 is duplicated (R1*) and connected with the stripping column S2. The streams are rerouted, so that the external vapor stream V^{ex} is transformed to an internal vapor stream

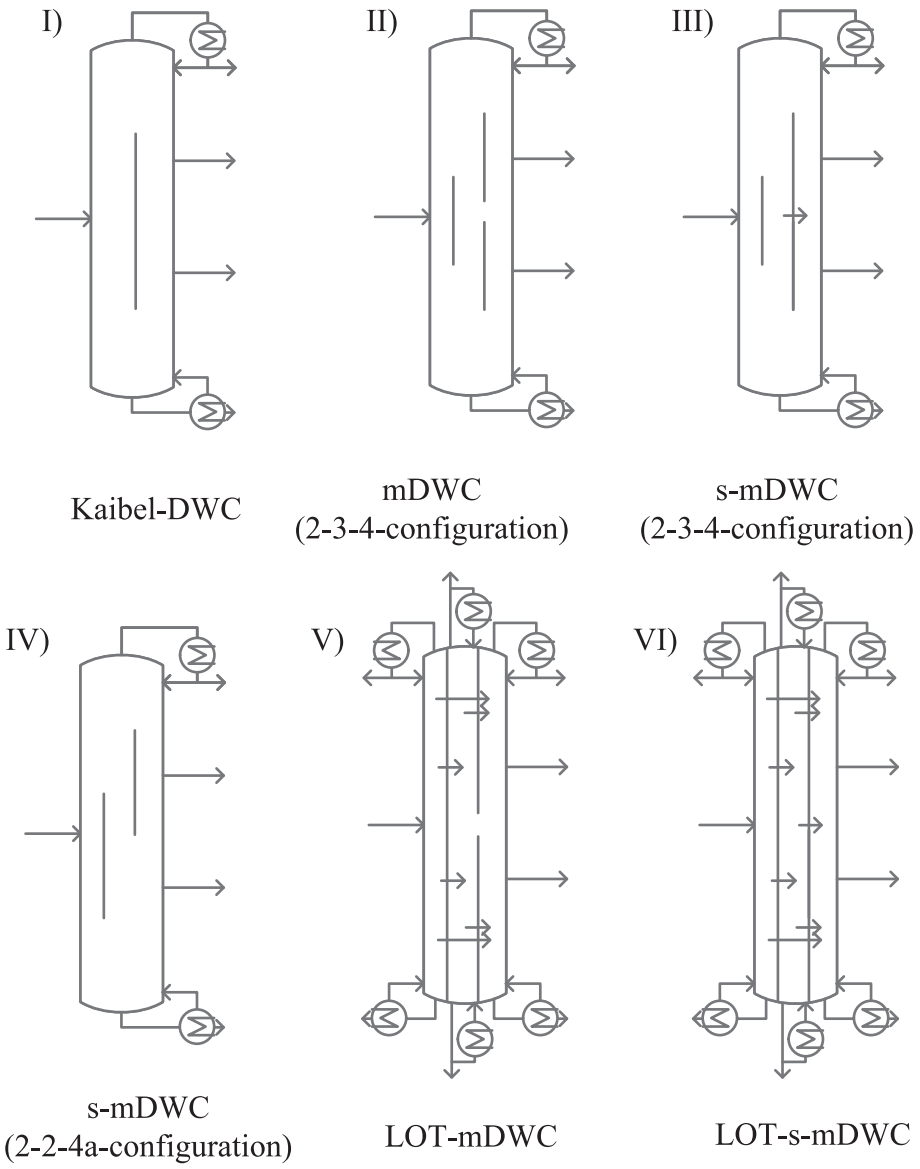

Fig. 7. Sketch of I) a Kaibel-DWC, II) a multiple dividing wall column mDWC in 2–3–4–configuration; III) a simplified version of the mDWC aka s-mDWC of the 2–3-4 configuration; IV) a simplified version of the mDWC termed 2–2-4a configuration; V) LOT-Version of the mDWC aka LOT-mDWC; VI) simplified version of the LOT-mDWC aka LOT-s-mDWC.

V^{ex2in}, now entering the duplicated section R1*. The stream L^{in} remains the same, however the liquid stream entering S2 is now composed from L^{ex} and the liquid stemming from the duplication R1*. Thus, the two columns are only connected via a liquid stream.

Based on this schematic, both external vapor transfer streams stemming from rectifying sections as well as stripping sections can be eliminated. For the TC-FC or the DWC, the LOT-procedure is shown in Fig. 6. Noticeably, the starting point of the TC-FC sequence is constructed differently than commonly shown (Fig. 1-(VIII)). However, the shown variation in Fig. 6 is thermodynamically equivalent with the rectifying section R1 shifted from the second column to the first, so that the LOT-development can be demonstrated in a straight forward manner (see e.g. Waltermann and Skiborowski [24]). For this, both the rectifying section of the first column (R1) as well as the stripping section of the second column (S2) are duplicated to R1* and S2*, respectively. In accordance with the LOT-methodic already discussed for the LOT-SR and LOT-SS, the vapor streams are rerouted from external vapor streams (V^{ex-up} and V^{ex-lo}, respectively) to internal vapor streams ($V^{ex2in-up}$ and $V^{ex2in-lo}$, respectively), leading into the duplications. Thus, a LOT-FC sequence consisting of two columns connected via two liquid side streams is obtained.

Ramapriya et al. [37] discussed the flexibility of this LOT-FC compared to the DWC and found that there are two aspects with respect to this comparison: First, DWCs have to be designed with the optimal vapor split in mind, which corresponds with the minimum vapor requirement for the desired separation (V_{min}). This has to be done, since the vapor split is essentially fixed during the design stage of the column, as already pointed out in the discussion in Section 1.1. In case of changing feed conditions, there is no guarantee to retain the optimal vapor distribution between the prefractionator and the main column. While it has been shown, that there is some leeway in the optimal vapor distribution [12], the extent of this termed “optimality region” (ΔV) strongly depends on the characteristics of the mixture to be separated. Ramapriya et al. [37] showed that this region can be quite narrow ($\Delta V/V_{min} < 1$ %) for some mixtures. While this calculation was based on constant relative volatilities and is as such only applicable to nearly ideal systems, it highlights a conceptual advantage of LOT-FCs and LOT–DWCs over DWCs, since the additional heat exchangers in the LOT-

version allow for a precise manipulation of the vapor streams in the columns and as such, robust operation in the optimality region is facilitated. The second flexibility aspect discussed by Ramapriya et al. [37] is that the LOT-FC can be utilized as an LOT–SR or LOT–SS without constructional measures, simply by not utilizing one of the liquid streams. This level of flexibility in already built plants cannot be provided in e.g. a DWC, however depending on the mode of production, it might add significant value, since the SR- or SS-configuration can be more efficient than the FC-configuration for changing feed conditions [14].

2.2. Enumeration and classification

The LOT-concept is applicable to every TC-connection and thus results in a variety of LOT-configurations. So far, LOT-sequences have been enumerated specifically up to quinary separations. The more substances are separated, the greater the variety of possible sequences, hence this subsection does not claim exhaustiveness but rather provides an overview over LOT-sequences discussed in the available literature. For the sake of efficient discussion, the components/products (*ABCDE*) will be numerated alphabetically in ascending order of boiling temperature with *A* being the lightest boiling component/product and *E* being the highest boiling component/product.

(I) Ternary separation (*ABC*)

The benchmark for a ternary separation in an uncoupled sequence is usually established by the DS consisting of two columns. For the TC- and LOT–systems, ternary separation sequences mainly include SR-, SS-, and FC-sequences and their LOT–variations. Two popular variations of the LOT–FC are obtained as combined sequences when only the rectifying section or the stripping section is developed to an LOT–section. If only the rectifying section is transformed, the sequence is termed LOT^{UP}–$T\text{-}C^{LO}$–FC* or LOT^{UP}–TC^{LO}–DWC* (Figure SI-2 in the Supplementary Information), if only the stripping section is transformed, the sequence is termed TC^{UP}–LOT^{LO}–FC* or TC^{UP}–LOT^{LO}–DWC* (Figure SI-2 in the Supplementary Information). These DWCs require the same heat duty as the original DWC, however are only marginally more expensive due to one additional heat exchanger. Ramapriya et al. [59] termed these LOT–DWCs “easy-to-operate” and summarized that they are characterized by having the dividing wall extended to at least one end, so that all internal streams can be controlled by external means. If the dividing wall is extended to the top, the internal streams, more precisely, the vapor split can be controlled by manipulating the individual pressure in the condensers. If the dividing wall is extended to the bottom, the internal streams can be manipulated via the easily controllable liquid split. If the dividing wall is extended to both ends, the internal streams can be manipulated by the liquid transfer streams.

(II) Quaternary separation (*ABCD*)

A quaternary separation in an uncoupled sequence is conducted in three columns. Oftentimes the direct sequence consisting of three columns (3-DS*: Figure SI-3 in the Supplementary Information) is used as a reference case. In order to perform a quaternary separation in a dividing wall column, either two side streams on a regular DWC with a single partition wall are necessary, which yields the Kaibel-DWC (Fig. 7-(I)), or multiple dividing walls in one column are used, which yields a multiple dividing wall column (mDWC). There are different ways of implementing these dividing walls, with the so called 2–3–4–configuration (Fig. 7-(II)) as the direct extrapolation of the fully-thermally coupled DWC for ternary separations. The mDWC has found great appeal in academic research due to its significant saving potential of up to 55 % [25,60], however industrial application is comparably slow with only one report of an industrial-scale dual dividing wall column to date, that has just been commissioned in the last year [34]. One of the main reasons for this is the challenging operation of a column with multiple vapor splits [37], which makes the mDWC a particularly interesting application case for an LOT-adaption. Agrawal [50] proposed an LOT-version of an mDWC with three condensers and three reboilers, where two vapor splits are eliminated, the vapor split where the two middle boiling components (*BC*) are transported remains (Fig. 7-(V)). This remaining intersection with bidirectional liquid and vapor split can be converted, by drawing a simplified version of the mDWC (s-mDWC), where the vapor split *BC* is replaced by a liquid stream as shown in Fig. 7-(III) [25]. It is important to note, that this simplification is not the same as the LOT-development, but a straight forward replacement of a liquid–vapor connection with a liquid connection. Hence, this s-mDWC is not thermodynamically equivalent to the regular mDWC, however, Ramapriya et al. [37] postulated that this regular and simplified DWC will have the same minimum energy demand for the majority of applications. This is substantiated by Ge et al. [61], who conducted an extensive study on the minimum vapor demand of different versions of s–mDWCs, including the 2–3–4–configuration and another simplified mDWC termed 2–2–4a–configuration which displays only two vapor splits (Fig. 7-(IV)). They found that depending on the feed characteristics, the simplified versions of the mDWC can display the same minimum vapor demand as the regular mDWC. The full LOT-transformation of the mDWC to e.g. the LOT–s–mDWC of the 2–3–4 configuration is illustrated in Fig. 7-(VI). This conversion results in a DWC with three full portioned parallel segments with seven liquid transfer streams, which is certainly a constructional and operational challenge, despite the possible flexibility.

The equivalent vapor demands of the 2–3-4 configuration of the mDWC and the s-mDWC were also investigated in a subsequent publication by Ramapriya et al. [59] through the comparison of their minimum energy demands obtained with the Global Minimization Algorithm [62] based on the Underwood equations for 120 different feed mixtures. In 94 % of the cases, the minimum energy demand was the same for the s-mDWC and the mDWC. Based on these findings, fourteen combined variants of the s-mDWC are enumerated where there are partially LOT-connections and partially conventional TC-connections up to the full LOT-s-mDWC (Fig. 7-(VI)). Depending on the amount and placement of the LOT-connections, this yields mDWCs with one to three condensers and reboilers, respectively. As with the ternary LOT-SR-DWC, the possible remaining vapor splits in these alternatives could be manipulated via the pressure in the respective condensers when the dividing walls extend to the top and are as such termed “easy-to-operate” [37,59]. Up to this point, separation always referred to a sharp split separation. Considering non-sharp separation of e.g. four components in an LOT-DWC with a single dividing wall and one or two (mixed) side streams significantly inflates the amount of possible separation sequences. Ramapriya et al. [37] showed twelve configurations: Respectively the body of an LOT-FC-DWC, an LOT–SR–DWC and an LOT–SR–DWC with either one mixed side stream (BC) or two side streams with different splits (*BC* and *C*, *B* and *BC* or *B* and *C*). In this case, the LOT–FC-DWC essentially marks the LOT–Kaibel–DWC. Considering that the body of the Kaibel–DWC is similar to that of the regular DWC, developing the Kaibel–DWC to an LOT–Kaibel–DWC is trivial, analogously to the development of the DWC to the LOT–FC-DWC as shown in subsection 2.1.

(III) Quinary Separation (*ABCDE*)

The considerations discussed for the quaternary case also apply to the quinary separation case, however complexity and amount of sequences increases further. For a sharp separation, the mDWC for a quinary separation (5-mDWC*: Figure SI-4 in the Supplementary Information) hosts six dividing walls, it can be transformed to a 5-LOT-mDWC* (Figure SI-4 in the Supplementary Information) with three remaining vapor splits at the gaps of the dividing walls where the middle boiling components are transported (*BCD*, *BC* and *CD*). Here again, a

simplified version of this 5-mDWC can be obtained, which would allow for a total elimination of vapor splits, albeit with a possible penalty on the minimum energy demand [63]. Furthermore, as discussed for the quaternary case, if non-sharp separations are included in the consideration, a quinary separation can also be conducted in e.g. an LOT-FC-DWC with three (mixed) side streams or an LOT-Kaibel-DWC with mixed side streams [37]. Here again, since the development of the body of the LOT-FC-DWC has already been discussed in detail in the previous subsection 2.1, the LOT-development is trivial. Furthermore, Ramapriya et al. [37] demonstrated how these mixed LOT-FC-DWCs can be extended to become LOT-mDWCs that produce pure products, by integrating an additional column including condenser and reboiler into the LOT-DWC, which is responsible for purifying one of the mixed side streams.

(IV) N-Product Separation

The methodology proposed by Ramapriya et al. [37,59] for enumerating LOT-DWCs, can be applied to an arbitrary number of components/products. However, it should be noted that with an increasing number of components/products, the number of vapor splits that cannot be eliminated without a simplification of the mDWC increases. Yet, these LOT-DWCs for more than five component separations are always significantly less complex than the original TC-DWCs.

2.3. Shortcut calculations and screening

Shortcut calculations are well-established in the field of distillation research and design, with one of the most well-known shortcut formulation being the Underwood equations, which provide a minimum reflux ratio or vapor duty of a given separation [64–66]. As already indicated in the previous section, shortcut computations on the basis of the Underwood equations have also been applied for LOT–configurations. While these shortcut methods provide a lot of flexibility and advanced model formulations suitable for global optimization [62], the Underwood equations rely on the assumption of constant molar overflow and constant relative volatilities. Consequently, these methods are well-suited for nearly ideal systems, but may show strong deviations for non-ideal mixtures. Jiang et al. [67] utilized these shortcut models in the context of a synthesis of thermally coupled sequences based on an extension of the matrix method by Sha and Agrawal [68]. They showed that LOT-versions of these synthesized TC-sequences are developed in a straight–forward manner to obtain “easy-to-operate” DWCs. The framework of a shortcut-based global optimization algorithm was

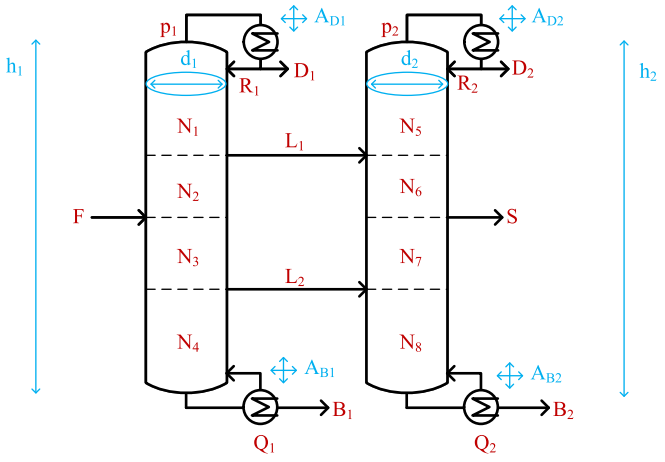

Fig. 8. Visualization of degrees of freedom (DOF) (red) and relevant dimensions (blue) for an LOT-FC sequence for the grassroot design. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

further extended towards an exergy-based evaluation of the considered process variants [69], as well as the Fenske equation and further correlations for size and cost estimation to yield a for total cost estimation as objective for the optimization [70]. The approach that combines an enumeration-based evaluation of the individual process configurations by means of specialized model formulations for global optimization enables a computationally efficient screening of several thousand thermally coupled and uncoupled sequences for a quinary separation which are then developed to LOT-sequences. While this extensive screening provides an excellent basis for decision making, it has to be recognized that no specific calculations are performed for the costs of LOT-sequences in comparison to their TC-counterparts. Chen and Agrawal [71] further employ the global optimization approach of Nallasivam et al. [72] for the classification of DWCs, which they categorize based on the location and extension of the dividing wall as well as the presence of LOT-streams over the dividing wall. The evaluation is performed for artificial ternary mixtures with different relative volatilities based on the computed minimum required vapor duty, covering a DWC, DWC–SR/DWC–SS, LOT^{UP}–TC^{LO}–FC/ TC^{UP}-LOT^{LO}–FC and a combined sequence with one end of the prefractionator in thermal coupling and the other end executed as a regular prefractionator sequence (PF^{UP}–TC^{LO}*/ PF^{UP}–TC^{LO}–DWC* and TC^{UP}–PF^{LO}*/ TC^{UP}–PF^{LO}–DWC* all sketched in Figure SI-5 in the Supplementary Information). The DWC/TC-FC and its LOT-variants always displayed the smallest minimum energy requirement, with the combined sequence often displaying a similar vapor duty and the DWC–SR/DWC–SS often being in the same range as the DWC. In more recent work the group of Agrawal and Tawarmalani proposed further extensions to relax the assumption of CMO [73] and replace the enumeration-based approach by a simultaneous optimization of a mixed-integer nonlinear programming problem [74]. They summarize their overall efforts on the synthesis and screening of energy-efficient distillation configurations in their recent review [75].

In order to fully overcome the limitations of the Underwood equations, a number of shortcut methods that avoid the assumption of constant molar overflow and constant relative volatilities can be applied [76]. These methods employ rigorous thermodynamic calculations for the vapor–liquid equilibrium and specific enthalpies in order to compute the minimum energy demand, based on the computation of the so-called pinch points, similar to the Underwood equations. The added complexity does however come with additional challenges, such that no similar approach to the global optimization approach has been proposed so far. Based on the Rectification Body Method [77,78], Brueggemann and Marquardt [79] first demonstrated the screening of simple sequences and TC-sequences for ternary separations. This was further extended to general three-product separations including further options with vapor recompression and multi-effect distillation by Skiborowski [80]. Based on the thermodynamic equivalence this screening is also applied for regular as well as heat-integrated LOT-sequences. This has been demonstrated for varying feed compositions for the separation of benzene, toluene and ethylbenzene [81] as well as hexanol, octanol and decanol [82]. The results will further be discussed in more detail in Section 5.1, focusing on the potential of heat-integrated LOT-sequences.

3. Conceptual design

The optimal design of regular distillation column sequences has been a focus of research for decades. Hence, an abundance of design strategies is available, extending from simulation-based methods employing commercial flowsheet simulators to rigorous optimizations by means of tailored superstructure models. Even though the design of an LOT-sequence involves determining additional degrees of freedom, the complexity of the design problem is not significantly larger, so that the methods used for regular and complex distillation column design can be applied to LOT-sequences as well. It is however important to make a distinction between design strategies used for grassroot design of an LOT-sequence (Section 3.1) and retrofitting uncoupled sequences to

LOT-sequences (Section 3.2). Although industrial interest in retrofitting methods is at least as large as it is in grassroot design, the latter has received considerably more attention.

3.1. Grassroot design

For the grassroot design of any distillation sequence, several discrete and continuous degrees of freedom (DOF) have to be determined in order to define the system. The number of DOF scales inter alia with the amount of side streams in the system, e.g. for the basic design of an LOT-FC, eight discrete DOF and nine continuous DOF have to be determined. While different combinations of defining DOF are possible, a common set of DOF for the LOT-FC is the discrete stage distribution in eight column sections $N_1 \ldots N_8$, as well as a set of continuous DOF covering the pressure of both columns (p_1 and p_2), the reflux ratios (R_1/D_1 and R_2/D_2), the liquid side streams (L_1, L_2 and S) and the heat duties of both columns (Q_1 and Q_2). This is visualized in Fig. 8. Due to the mixed nature of DOF and the nonlinear thermodynamic relations in the distillation process, optimal column design problems are usually stated as mixed integer nonlinear programming problem (MINLP), thus requiring sophisticated design methods. Individual DOF can be fixed before the design procedure in order to streamline the problem, e.g. specifying the pressure at a sensible value. Based on the basic design, key performance factors of the sequence like overall heat duty (Q_{total}) and stage count (N_{total}) can be assessed and compared to alternative sequences. In order to take into account tangible economic aspects, column dimensions have to be considered. The column diameters (d_1 and d_2) are generally determined based on a maximum vapor velocity related to the column internals. The column heights (h_1 and h_2) are calculated based on the column stage count considering the tray efficiency in tray columns or the height equivalent per theoretical stage (HETP) in packed columns. The size of heat exchangers (A_{D1}, A_{D2}, A_{B1} and A_{B2}) correlate with the required heat/cooling duty as well as the temperature difference. Operational costs OPEX and investment CAPEX for a given sequence are calculated based on the respective size estimations as well as the operating variables. These costs are condensed into the total annualized costs (TAC). Refer to the article of Waltermann et al. [25] for a more elaborate discussion on the DOF and the respective models for an economic optimization of DWC and LOT-DWC configurations.

So far, a number of grassroot design studies was conducted for different forms of LOT-sequences, which are categorized in this contribution into equivalence-based design (design with stage distribution based on TC-sequences) and direct design approaches (rigorous designs with independent stage distributions).

Equivalence-based designs are developed on the basis of a TC-configuration by direct duplication of the respective column sections including their respective stage counts. This essentially follows the practical application of the synthesis approach discussed in Section 2. The duplication is followed by a minimization of the required heat duty Q_{total} or operational costs in order to determine the optimal operating point for the equivalence-based sequence. Next to its simplicity, this approach has the benefit of providing direct comparability of TC- and LOT-sequences, which is why it is mainly applied in studies that conduct a direct comparison of LOT-sequences with their TC-counterparts, either in terms of controllability [83–88], thermodynamic efficiency [84] or in terms of energy demand equivalence [56,89]. While in some of these equivalent-based designs, the energetic equivalence is effectively demonstrated, other designs results in a significant difference in the energy demand of the LOT- and the TC-sequence, which should not be the case for optimal designs due to the thermodynamic equivalence, unless the investment cost estimates for the DWC and the LOT-sequence are significantly different. E.g. Segovia-Hernández et al. [84] note that while some of the investigated designs in their case study display almost the same energy requirement (<0.5 %), in other cases there is an apparent difference in energy requirement (>7%).

In comparison to the equivalence-based design approach, direct design approaches adhere to the inherent MINLP-nature of distillation design via a tailored optimization strategy. So far, the strategies applied for LOT-sequences can be categorized into sequential simulation-based optimization, considering sequential-iterative, stochastic and multi-objective optimization, as well as simultaneous optimization frameworks based on specific superstructure models. While the former build on respective column configurations implemented in a commercial process flowsheet simulator, such as Aspen Plus, the latter builds on a tailored equation-based model formulation that enables direct application of equation-oriented (MI)NLP solvers.

Wu et al. [90]. implemented a sequential iterative design strategy for the design of an LOT-FC based on an Aspen Plus simulation with Radfrac models with NRTL (Nonrandom-two-liquid-model) as liquid phase activity model. The sequential iterative approach involves an iterative loop of adjusting the stage distributions and consecutively optimizing the continuous DOF in order to reduce the TAC of the sequence. They showed that with this iterative design strategy, the designed LOT-FC for the separation of an equimolar mixture of 1,2-ethandiol, 1,3-propandiol and 1,4-butanediol requires 7 % more investment than the DS. However, since the operational costs were reduced by 19 % with the LOT-FC, the TAC of the LOT-FC were 17 % lower than those of the DS, thus constituting the more economic sequence for this separation. While this approach proved to be effective, it has to be noted that it does not guarantee determining even a local optimum in respect to the TAC.

In order to overcome the limitation of manual adjustment without necessitating derivative information, metaheuristics were applied for a stochastic optimization on the basis of a simulation model, e.g. by means of the self-adapting dynamic evolution algorithm (SADDE) [51,91,92] and the mesh adaptive direct search (MADS) for several designs [52,93]. Cui et al. [91] applied SADDE, implemented in Matlab and linked to Aspen Plus Radfrac models, to optimize the design of the LOT-SR, LOT-SS, LOT-FC as well as combined sequences where the lower part of the LOT–SR is combined with the upper part of the PF–sequence (PF^{UP}-LOT^{LO}*; Figure SI-6 in the Supplementary Information) and the upper part of the LOT–SS is combined with the lower part of the PF–sequence (LOT^{UP}–PF^{LO}*; Figure SI-6 in the Supplementary Information). For an equimolar mixture of benzene, toluene and xylene (BTX), the LOT–FC demanded the lowest reboiler duty. In terms of TAC, the combined PF^{UP}–LOT^{LO} and the LOT–FC displayed almost the same costs, with the PF^{UP}–LOT^{LO} displaying marginally fewer overall costs (–0.4 %). The same methodology was applied again in a subsequent publication of the same authors for the LOT–FC, again with the TAC as the objective [51]. Yet, since this publication focused primarily on control, no comparison to other sequences was conducted. Feng et al. [52,93] also optimized the LOT–FC for the separation of ethanol, propanol and butanol using the MADS algorithm for optimization linked to Aspen Plus Radfrac models for simulation. Besides a control analysis [93] the authors performed an exergetic analysis of the LOT–FC design with the regular DWC as a reference [52]. In this case study, the DWC require less investment costs, yet significantly higher operating costs than the LOT-FC. Overall, this results in a TAC reduction of the LOT-FC of 11 % when compared to the DWC. In terms of exergetic efficiency, the LOT-FC displayed an efficiency of 11 %, whereas the DWC displayed an efficiency of just 9 %. Based on these results, the authors conclude that the LOT-FC is attractive both in terms of economy as well as exergy. However, it should be noted that direct comparability between these two sequences is limited, given that the authors remark that the DWC is not at the energy-minimal operating point after the TAC-optimization.

Kong et al. [92] utilized the SADDE-algorithm with Aspen Plus (Radfrac) for the design of the LOT–Kaibel–FC and used the three-column-DS (3-DS) as a reference. While the overall heat duty of the LOT-Kaibel-FC was approximately 19 % less than that of the 3-DS, the TAC was only reduced by 12 %. Even though the LOT-Kaibel-FC requires only two columns, whereas the 3-DS requires three columns, this can be explained by the different boiling temperatures requiring different steam levels. Firstly, the LOT-Kaibel-FC evaporates exclusively at the

high boiler boiling temperature, whereas for the 3-DS, only the third column evaporates high boiler. Furthermore, in this publication, the pressure was used as a DOF during the optimization, resulting in a higher pressure in the LOT-Kaibel-FC columns, so that a more expensive steam utility has to be utilized. This is an important factor that generally needs to be considered for thermally coupled processes in comparison with uncoupled sequences.

Stochastic optimization can also be applied for multi-objective optimization, which has been conducted for the LOT-FC for ternary separations, as well as the LOT-Kaibel-FC and a LOT-mDWC for a quaternary separation. Liu et al. [94] optimized the design of the LOT-FC with a multi-objective genetic algorithm in MATLAB linked to an Aspen Plus Radfrac model. They further considered a constraint on the number of stages in adjacent columns sections, in order to facilitate an easy transfer to the LOT–FC–DWC design. The individual objectives were the minimization of the overall number of stages and the minimization of the overall heat duty. For the BTX separation, one of the non-dominated solutions on the resulting pareto front yielded a reduction of 30 % of the heat duty and 19 % of the TAC compared to a conventional distillation sequence. Yet, it was not specified which conventional sequence they were referring to, specifically.

For the LOT-Kaibel-FC, Zhang et al. [95] performed a multi-objective optimization by means of the non-dominated sorting genetic algorithm NSGA-II linked to an Aspen Plus model for the separation of methanol, ethanol, propanol and butanol. The optimization objectives were again the minimization of the overall number of stages and the minimization of the overall heat duty. The authors note, that these metrics are not direct representatives for OPEX and CAPEX, since a high number of stages is correlated with a high column shell, but also yields smaller heat exchangers and a smaller column diameter. Therefore, the TAC is considered as additional objective and the solution with the lowest TAC was identified from the set of non-dominated solutions from the pareto front. This design was subject to further controllability investigations. Li et al. [96] also utilized the NSGA-II algorithm for calculating pareto optimal solutions of the LOT-s-mDWC for the separation of methanol, ethanol, propanol and butanol, considering the same objective functions. They further modified the simulations in Aspen Plus, such that product purities were enforced through Aspen Plus' Design Specs. Li et al. [96] report a reduction of the required reboiler duty by 39 % and in TAC by 37 % for the LOT-s-mDWC compared to a conventional sequence. However, it is again not specified which sequence is considered as the reference.

These publications demonstrate the possibilities to optimize different LOT-configurations for ternary and quaternary separations building on

Table 1
Overview of applied grassroot design strategies for different LOT-sequences (For the sake of completeness, studies that focus on control are listed as well, although they often do not have a reference sequence).

LOT-Sequence	Substance System	Design Strategy	Process Model	Saving Potential of Key Sequence Q. Heat duty; CAPEX. Investment; OPEX. Operational cost; TAC. Total annualized cost	Source
LOT-FC	1,2-Ethandiol; 1,3-Propandiol; 1,4-Butanediol;	Sequential Iteration	Aspen Plus Radfrac with NRTL	CAPEX. + **7 %** (Ref. DS) OPEX. −**19 %** (Ref. DS) TAC. −**17 %** (Ref. DS)	[90]
LOT-Kaibel-FC	Benzene; Toluene Xylene; Trimethylbenzene;	Stochastic Optimization via SADDE	Aspen Plus Radfrac with NRTL-RK	Q. −**19 %** (Ref. 3-DS) TAC. −**12 %** (Ref. 3-DS)	[92]
LOT-SR LOT-SS LOT-FC LOT-SR-PF LOT-SS-PF	Benzene; Toluene; Xylene	Stochastic Optimization via SADDE	Aspen Plus Radfrac with NRTL-RK	OPEX. LOT-FC ~ **-17 %** (Ref. DS) – taken from figure TAC. LOT-FC ~ **-6%** (Ref. DS) – taken from figure	[91]
LOT-FC	Benzene; Toluene; Xylene	Stochastic Optimization via SADDE	Aspen Plus Radfrac with NRTL-RK	No Ref.	[51]
LOT-SR-DWC LOT-SS-DWC LOT-FC-DWC	Mix 1. n-Butane; n-Pentane; n-Heptane. Mix 2. Acetone; Methanol; Water	Superstructure optimization	Rigorous MESH-based column formulation in GAMSWith NRTL (Mix1) & UNIQUAC (Mix2)	Mix1: TAC. LOT-FC-DWC + **4 %** (Ref. DWC) Mix2: TAC. LOT-FC-DWC + **4 %** (Ref. DWC)	[25]
LOT-Kaibel-FC	Methanol; Ethanol; Propanol; Butanol	Multiobjective Optimization via NSGA-II	Aspen Plus Radfrac with WILSON	No Ref.	[95]
LOT-FC	Benzene; Toluene; Xylene;	Multiobjective Optimization via genetic algorithm	Aspen Plus Radfrac with CHAO-SEAD	Q. −**30 %** (Ref. "conventional processes") TAC. −**19 %** (Ref. "conventional processes")	[94]
LOT-s-mFC	Methanol; Ethanol; Propanol; Butanol	Multiobjective Optimization via NSGA-II	Aspen Plus Radfrac	Q. −**39 %** (Ref. "conventional processes") TAC. −**37 %** (Ref. "conventional processes")	[96]
LOT-FC	Ethanol; Propanol; Butanol	Stochastic Optimization via MADS	Aspen Plus with NRTL	No Ref.	[93]
LOT-FC	Ethanol; Propanol; Butanol	Stochastic Optimization via MADS	Aspen Plus with NRTL	TAC. −**11 %** (Ref. DWC)	[52]

and exploiting a commercial process simulator, indicating possible energy and cost savings of up to 37 % compared to conventional sequences. However, especially with regards to the optimization it has to be noted that most of the publications do not report on the computational effort.

In order to overcome the limitations of a sequential optimization of a simulation model, dedicated superstructure models can be formulated and solved by means of gradient-based (MI)NLP solvers. The initial superstructure formulations for distillation column design were proposed by Viswanathan and Grossmann [97,98] and later extended to DWC designs by Dünnebier and Pantelides [99]. A more elaborate overview of the developments for DWC is provided in the review article of Waltermann and Skiborowski [24]. The authors also provide an illustration of the transferability of the results from the simultaneous optimization of a superstructure model on the basis of rigorous MESH models (Mass balance, equilibrium relation, Summation equation, energy balance) for the individual equilibrium stages to an Aspen Plus Radfrac simulation. Waltermann et al. [25] further extended the superstructure model and the simultaneous optimization to mDWC and LOT-DWCs, solving the resulting MINLP problems as a series of successively relaxed NLP problems. They compare the results of an economic optimization of the regular DWC, with two combined sequences where the upper or lower thermal coupling of a DWC is replaced by an LOT-module (LOT^{UP}-TC^{LO}-DWC* and TC^{UP}–LOT^{LO}–DWC* as shown in Figure SI-2 in the Supplementary Information) as well as the LOT–FC–DWC, for two case studies. This includes the separation of a zeotropic ternary mixture of n-butane, n-pentane and n-heptane, as well as an azeotropic ternary mixture of acetone, methanol and water. In both cases, the minimum energy demand for the DWC and LOT-DWC designs with equivalent stage distributions was virtually equivalent (<0.1 %), emphasizing the thermodynamic equivalence of the sequences. In terms of the economic optimization, the regular DWC displayed the smallest TAC, yet, the LOT-configurations required only a marginal cost increase of < 5 %. This perfectly aligns with the expectations, due to the thermodynamic equivalence of the sequences and the necessity of additional heat exchangers for the implementation of the LOT-configurations. This underlines the validity of the obtained results, that reportedly required only 10 min of computational time. Besides these computational benefits, the superstructure optimization is also comparably flexible and effectively integrates inequality constraints in the optimization problem.

Overall, a vast variety of design methods for grassroot design of LOT-sequences have been proposed in literature, where the majority builds on commercial process simulators. The key information on the different publications, design methods and reported saving potentials is summarized in Table 1. It should be noted, that the individual saving potential strongly depends on a number of factors including substance system, feed composition and cost correlation, assuming that each method identified the optimal designs. Furthermore, the sequence that is used as a reference is not the same in all publications and some lack a comprehensive description of the reference case, which further skews comparability. Hence, the reported saving potentials should not be considered as general heuristics, they merely provide an order of magnitude in which saving can be expected. Within the publications discussed in this section, this is 6–19 % of TAC for a ternary separation when compared to a regular sequence and 12–37 % for a quaternary separation when compared to a regular sequence.

3.2. Retrofit design

Unlike grassroot design, retrofit design has received only marginal attention so far. When retrofitting an uncoupled distillation sequence to an LOT-sequence, in principle the same DOF like in the grassroot design have to be determined, however the existing equipment imposes constraints on the column and heat exchanger sizes that need to be taken into account. More precisely, the desired purity has to be met within a limited amount of separation stages and the design has to stay within a hydraulic operational window defined by the existing column dimensions and internals. Considering that both the HETP as well as the tray efficiency depend on a number of variables, that possibly change during retrofit like e.g. the pressure or F-Factor, the number of theoretical stages per height may change during retrofit. In order to find an optimal design that minimizes the required energy duty, while satisfying purity, size and operational constraints, sophisticated model-based methods are required. The easiest, quickest and least expensive retrofit would include the implementation of one or more liquid side streams to transform an uncoupled sequence to an LOT-sequence, while keeping the column heights, diameters and heat exchanger areas unchanged. This is exemplarily illustrated for the LOT-FC configuration in Fig. 9. In case such retrofit is not feasible or economically sensible, changing the column internals or extending column sections for more separation stages or adding additional or larger heat exchangers are further options for a more extensive retrofit.

Even though retrofitting of unintegrated columns to thermally coupled columns or even DWCs is not generally a new concept [100,101], so far retrofit designs of LOT-sequences have received only very limited attention. Horsch et al. [102] propose an adaption of the superstructure optimization used by Skiborowski for grassroot design [81], which similar to the work of Waltermann et al. [25] applies a simultaneous optimization. The retrofit model includes additional constraints for pressure drop and separation efficiency, linking both to the F-Factor in the fixed equipment sizes. In the exemplary case study for the separation of a BTX mixture, it was demonstrated, that the operational costs can be reduced by 6–20 % by a tailored LOT-retrofit, depending on the feed composition. While a simple retrofit by introducing liquid side streams was not sufficient and additional heat exchanger area had to provided, the substantial energy savings, enable short payout times between 1.3–2.2 years. Apart from this optimization-based retrofit, other studies mention the possibility of retrofits based on similar column stage counts in the uncoupled designs and LOT-designs as well [57], however merely as an interesting opportunity without dedicated retrofit calculations. Furthermore, Kong et al. [103] perform a simulation-based retrofit estimation via a simple transfer of column stage counts from the uncoupled sequence to the LOT-sequence. Here, the retrofit required approximately 10 % less energy compared to the uncoupled sequence. Yet, it is important to note that in this instance, there is no specific mention of hydrodynamic constraints or separation efficiency, which are important factors for a detailed feasibility evaluation. Due to these promising exemplary results and the scarcity of research conducted on this specific topic, retrofit appears to be an important research area for advancing industrial implementation of LOT-sequences in the future.

4. Operation and control

One of the main arguments for the LOT-configuration raised in literature is the improved controllability due to the avoidance of the vapor split and additional DOF for the operation, which is why a number of studies was carried out on the steady-state and dynamic process behavior of LOT-sequences. So far, these studies can be divided into two categories: studies on the theoretical operability characteristics of LOT-sequences (cf. Section 4.1) and case studies with specific control systems for different LOT-designs (cf. Section 4.2). The hypothesis that internal vapor flows in column sections can be controlled more precisely with LOT-sequences due to only controllable liquid streams/splits and additional manipulate variables, which might support the operation at the energy optimal operating point has not yet been studied in detail. Furthermore, there are several studies on control of LOT-sequences with further process integration like reactive or extractive LOT-distillation sequences. These are not considered in the subsequent discussion, but are addressed in further detail in Section 5.

The goal of controlling distillation sequences is to operate the columns in a safe and resilient way, keeping the product specification despite possible disturbances. In order to do so, a number of manipulated variables (MVs) is changed in a targeted manner to keep control

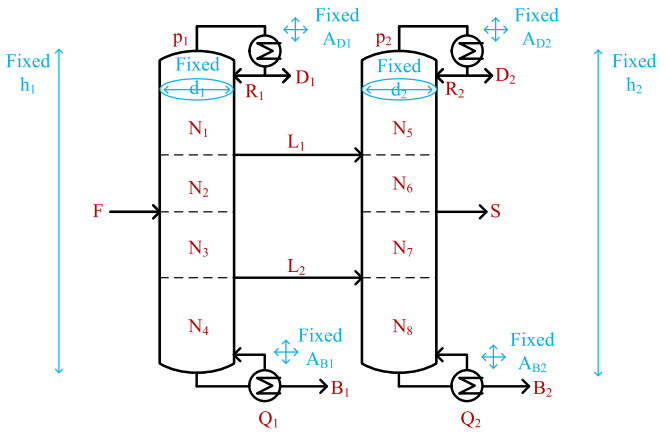

Fig. 9. Visualization of degrees of freedom (DOF) (red) and constraint dimensions (blue) for an LOT-FC sequence for the retrofit design. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

variables (CVs) at their setpoints. With distillation columns, there is one important distinction in terms of CVs: When the specification is controlled directly, the concentrations of the product streams serve as CVs. While this guarantees a precise determination of the column specification, online concentration measurement is usually expensive and comparably complex. It requires either spectroscopic measurements or online gas or liquid chromatography, which usually introduce a considerable time-delay. Industrial practice still commonly relies on temperature measurements in the column for stabilizing control. This allows for quick, robust and inexpensive measurements. Denomination of MVs and CVs is not always consistent when comparing different publications. For the sake of clarity, the denomination illustrated in Fig. 10 will be used for the discussion of control and operation. As an example, the LOT-Kaibel-FC is used, the number of side streams scales with the respective sequence. Possible MVs are the distillate streams (D_1 and D_2), the reflux streams (R_1 and R_2), the liquid side streams (L_1, L_2 and S_1, S_2), the ratio of liquid side stream to internal liquid stream (α_1, α_2 and β_1, β_2) and the heat duties (Q_1 and Q_2). Note that the manipulation of the respective ratios does either require the measurement and control of the internal liquid streams, which would be a considerable practical challenge or an external pump around system including ratio control, which is also more complex and expensive in comparison to a single pump. While technically, the bottom streams could serve as MVs for specification control as well, they are more commonly utilized for level control in the sump of the column [104]. Level control in the distillate vessel of the column is either conducted with the reflux R or the distillate D, depending on the operating point. For CVs, either the concentration of the respective key components or key impurities of the product streams and side streams (x_{D1}, x_{D2}, x_{L1}, x_{L2}, x_{B1}, x_{B2}, x_{S1} and x_{S2}) are used or the temperature or composition within the column on specific column stages (T_{1-1}…T_{1-N} or x_{1-1}…x_{1-N} for column 1 and T_{2-1}…T_{2-N} or x_{2-1}…x_{2-N} for column 2).

A number of control engineering metrics is calculated habitually to support the generation of control systems as well as to provide means of quantitatively comparing the controllability of processes or quality of control systems. In the following these metrics are referred to as slope criterion, sensitivity criterion and balance criterion. The slope criterion is applied, if a specific CV within the column has to be determined (T_{1-1}…T_{1-N} or x_{1-1}…x_{1-N}, T_{2-1}…T_{2-N} or x_{2-1}…x_{2-N}). The temperature or concentration slope with respect to the stage count is calculated. It is recommended to use a stage that displays a high slope, since this stage is more sensitive to changing conditions. In order to consider the sensitivity- and balance criterion, the relation of all relevant manipulated and control variables is represented by either the steady state sensitivity matrix G_{SS} or a dynamic transfer function matrix G_{TF}. While this can be

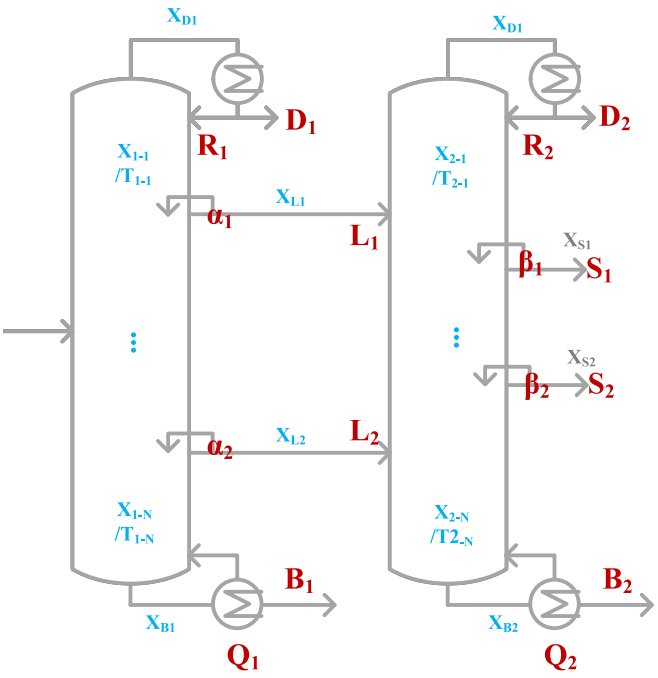

Fig. 10. Illustration of possible manipulated variables (MVs) in red font and control variables (CVs) in blue font for the LOT–Kaibel–FC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

used directly do identify sensible control loop pairings, for multivariable control systems it is recommended to conduct a singular value decomposition of the matrix for a quantitative evaluation of the sensitivity- and balance criterion.

$$G_{SS/TF} = U \bullet \Sigma \bullet V^T$$

The sensitivity criterion is represented by the minimum singular value of Σ, which is σ_{min}. It offers information about the minimal CV-to-MV-sensitivity in the control system. The condition number constitutes the ratio of the maximum and minimum singular value, σ_{max} and σ_{min} respectively and denotes the balance criterion. In general, a high value for σ_{min} and a small condition number are considered favorable for control, since this presents a balanced system with high sensitivities. In contrast, small values for σ_{min} and consequently high values of the condition number might indicate that at least one of the manipulated variables should not actually be utilized within the control system. An extensive discussion of these criteria is provided in the book of Luyben [105].

4.1. Theoretical operability

Ramírez and Jiménez [83] first investigated the operability of the LOT-SR and the LOT-SS by means of rigorous simulation, based on a modelling procedure provided by Hérnandez and Jiménez [106], and compared them to their TC-counterparts. Three substance systems with varying ease-of-separation index were selected for analysis: N-pentane, n-hexane, n-heptane, as well as n-butane, *iso*-pentane, n-pentane and *iso*-pentane, n-pentane and n-hexane. Based on a qualitative assessment of the visualized sensitivity of the required heat duty on the liquid and vapor transfer streams, they conclude that the LOT-sequence is more sensitive to changing conditions than its TC-counterpart. It should be noted, that in this analysis, the intercolumn vapor stream of the TC-sequence is changed during the energy optimization. While this is a sensible choice during the design stage, it might in fact only be a limited option during operation, as discussed in Section 1. This study sets a

benchmark for operability considerations of LOT-sequences, since all of the studies discussed in this subsection utilize the same substance systems, the same feed conditions and the same sequences in computational studies, which should make the results comparable.

Segovia-Hernández et al. [84] modelled the LOT-SR, LOT-SS and their respective TC-counterparts in Aspen Dynamics in order to calculate and compare the sensitivity and balance criterion based on the transfer function matrix G_{TF}. They found that the LOT-sequences consistently show lower minimum singular values σ_{min} and higher condition numbers than the TC-counterparts for all of the considered mixtures, indicating that the LOT-sequences actually displayed worse theoretical control characteristics than the TC-sequences. A low σ_{min} and subsequently a high condition number can indicate that individual MVs should not be included in the control scheme [107]. However, it has to be noted that the study does not specifically state which MVs and CVs where considered for the singular value decomposition analysis, so that it cannot be conclusively determined which control loop should be eliminated in the LOT-sequence. Alcántara-Ávila et al. [87] performed a very similar study for the same sequences by means of Aspen Dynamics models. They concluded the same results in terms of controllability, supporting the conclusions of Segovia-Hernández et al. [84]. However, similar to the previous study, it was not stated specifically which variables were used for the singular value decomposition analysis. Furthermore, the sensitivity of the required heat duty on the transfer streams was assessed qualitatively and since the required heat duty of the TC-sequence does not depend on the transfer stream as much, it was concluded that the TC-sequence would be more easily controlled, further supporting the findings of Ramírez and Jiménez [83]. Thus, these initial studies actually indicated a comparably worse theoretical operability of the LOT-sequences when compared to the TC-sequences.

Based on these initial studies on the steady state gains, Segovia-Hernández et al. [85] extended their analysis for the LOT-SR, LOT-SS and their respective TC-counterparts on a broader frequency band. In order to obtain dynamic data, the sequences were simulated in Aspen Dynamics. Here again, the minimum singular value σ_{min} and condition number were determined. The MVs for the LOT-sequences were both heat duties Q_1 and Q_2 and both reflux ratios RR_1 and RR_2. For the TC-SR both reflux ratios RR_1 and RR_2 and the heat duty Q were considered, for the TC-SS both heat duties Q_1 and Q_2 and the reflux ratio RR. The CVs were the compositions of all product streams. Based on this analysis, it was concluded that the LOT-SR shows better control metrics for a broad frequency range than the TC-SR and the TC-SS shows better control metrics than the LOT-SS. In this case, the authors selected a control system for their analysis that does not include the liquid side streams of the LOT–sequences or the TC–SS. Since it is suggested that the controllable liquid stream might provide significant advantages in terms of flexibility, it would be an interesting next step to include this manipulated variable into theoretical control analysis in the future. This study was further supported by Tamayo-Galvan et al. [86], who concluded the same results based on the same control engineering metrics stating that the LOT-SR is easier to control than the TC-SR and the other way around for the SS-configurations for a majority of the frequency band.

Concluding this subsection, a number of studies has been conducted on theoretical control characteristics of the single coupled LOT-SR and LOT-SS in comparison with their TC-counterparts. So far, no studies have been conducted on the LOT-FC or more complex sequences. Furthermore, none of the studies conducted so far, explicitly investigated the influence of the liquid side stream as a manipulated variable on the controllability of the process. It should be noted that while these general controllability metrics are first valuable indicators, they only represent open loop behavior. In order to conclusively asses the control characteristics of a process, interaction metrics have to be considered e. g. in terms of a relative gain array analysis and ultimately dynamic studies have to be conducted. The latter are subject of the following section, but have not yet been applied on LOT-SR and LOT-SS configurations.

4.2. Dynamic control analysis

A number of contributions are dedicated towards the implementation of specific control systems for the LOT-FC, the LOT-Kaibel-FC and the LOT-mDWC for different separation cases. Cui et al. [51] investigated the control of an LOT-FC for the separation of BTX based on Aspen Dynamics simulations, by analyzing the dynamic behavior of the process at a ± 20 % disturbance of the throughput and the feed composition for six different control systems that are distinct by the choice of CVs and the architecture of the control system. For composition control (CC), they considered a control system with the key impurities in the respective streams as CVs. For a quicker control, three different control architectures including ratio controllers that introduce feedforward action are considered, which improved the dynamic performance compared to the original CC-system. For the temperature control (TEMPC) system, regular temperature control loops are applied. Since both heat duties (Q_1 and Q_2) only influence the column temperature profiles marginally, the heat duties are not utilized for regular temperature loops, but rather within the ratio controllers Q_1 / F, relating the heat duty Q_1 to the feed F and a feedback ratio controller Q_2 /S for the heat duty Q_2 and the side stream of the second column S. The CV positions here were determined based on the steady state sensitivity G_{ss}. For smaller disturbances (±10 % throughput), this rather complex control system solely relaying on temperature measurements provided a good dynamic performance and only displayed marginal composition offsets. However, for bigger disturbances, the column specification cannot be maintained and thus, a TEMPC-system amended by one composition controller in order to maintain the neuralgic composition was proposed and deemed the most industrially advantageous system. Feng et al. [93] also investigated the control of the LOT-FC based on Aspen Dynamics simulations for a disturbance of ± 20 % in throughput and composition. They did this for the separation of ethanol, propanol and butanol and compared TEMPC-systems with different architectures. The sensitivity criterion is applied for CV-placement and a relative gain array analysis is conducted for control loop pairing. Regular temperature control loops are applied to the two distillate streams D_1 and D_2 as well as the reboiler duty of the first column Q_1 and the side stream of the second column S. Furthermore, instead of directly controlling the liquid side streams of the first column, L_1 and L_2 respectively, the authors controlled the liquid ratio of side stream to the internal liquid stream α_1 and α_2, respectively. The sum of α_1 and α_2 was input to a ratio controller, controlling the reboiler duty of the second column Q_2. Two further variants of this basic TEMPC-scheme were compared as well, including one variant with ratio controllers and one variant with temperature difference controllers. They concluded that out of the investigated control schemes, the TEMPC-system including temperature difference controllers performed the best. The control of the LOT-FC was further investigated by Liu et al. [94] for BTX for a throughput and composition disturbance of ± 10 % and ± 20 %. They compared four control systems: Two systems where the liquid side streams (L_1 and L_2) were used as MV (one CC-system and one TEMPC-system, respectively) and two systems where the liquid ratio of side streams (α_1 and α_2) were utilized as MV (one CC-system and one TEMPC-system respectively). A singular value decomposition was conducted in order to identify suitable temperature stages for control. Both the CC– as well as the TEMPC system that utilize L_1 and L_2 handled a small throughput disturbance of ± 10 % with acceptable oscillation and offsets and failed to handle larger disturbances of ± 20 %. In contrast, the CC-scheme with the liquid ratios α_1 and α_2 as MV successfully controlled even disturbances of ± 20 %, the TEMPC-scheme with the liquid ratios α_1 and α_2 as MV also controlled disturbances up to ± 15 %. A ± 20 % disturbance for this TEMPC-scheme was not attempted in this publication. The authors concluded that for their specific case study the control systems including the liquid ratios α_1 and α_2 provided better results than the schemes including the

liquid streams directly. However, as previously stated such a control would require an accurate measurement of the internal liquid streams. Furthermore, they recommended the TEMPC-scheme for industrial application, due to its reasonable performance in combination with inexpensive easy implementation. It should be noted, that this TEMPC-system also included a ratio controller on the feed and the heat duty of the first column F/Q_1, which introduced feed forward action to the control system. The other control systems in comparison were implemented without ratio controllers on the feed.

Kong et al. [92] analyzed the control behavior of the LOT-Kaibel-FC and compared it to the control performance of the 3-DS. Both processes were modelled in Aspen Dynamics for the separation of benzene, toluene, xylene and trimethylbenzene. The authors established a CC-system, a TEMPC-system and a hybrid TEMPC-CC-system. For the CC-system, the authors stated that utilizing the composition of the product streams did not yield sufficiently good results, which is why the compositions on eight selected column stages were used as control variables based on a sensitivity study to receive G_{SS}. Additionally, in order to guarantee tight control of all product specifications, a cascade controller adjusting the setpoint of one of the stage compositions in the first column as well as several ratio controllers on the feed and side streams were added. The 3-DS was controlled via a conventional two-point control system with the reflux and heat duty, supported by six feed forward controllers. Both processes were successfully controlled with the proposed control systems, the authors concluded that qualitatively, the controllability of the LOT-Kaibel-FC is comparable to that of the 3-DS-sequence. Considering the complexity of the Kaibel-configuration compared to the 3-DS, this substantiates an advantage in terms of controllability of the LOT-configurations. For the TEMPC-system, the temperature slope and the sensitivity criterion constituted by G_{SS} were calculated in order to select appropriate stages for temperature control. The distillate D_1, the side streams of the first column L_1 and L_2 as well as the side streams of the second column S_1 and S_2 were utilized as MVs. The heat duties Q_1 and Q_2 are not used directly within temperature control loops, since they exhibit a significant impact on multiple column stages that were also used within the other control loops. A relative gain array analysis to quantify possible interactions was not discussed. Rather, the heat duties are utilized within a ratio control (F/Q_1) and a feedback ratio controller (S_2/Q_2). The TEMPC-scheme displays smooth behavior with little oscillation, however for bigger disturbances (±20 %), composition offsets remain. In order to tackle this issue, three composition controllers were added to the TEMPC-system, resulting in a control system that controls all compositions sufficiently. This study supports the results for the LOT-FC by Cui et al. [51], concluding that a hybrid control system proved to be the most practical option. Zhang et al. [95] also investigated the control of an LOT-Kaibel-FC for the separation of methanol, ethanol, propanol and butanol. They implemented a CC-system, and two TEMPC-systems. One TEMPC-system was constructed with regular temperature control loops, one was amended by temperature-difference control loops. The temperature stages are determined based on the sensitivity criterion. The performance of the control system was tested for ± 10 % disturbance in the column throughput and the feed composition. The throughput disturbance is easily controlled with the CC-system, whereas the composition disturbance results in small remaining control offsets. With the regular TEMPC-system, the disturbances could be controlled, however with multiple remaining steady state offsets. The overall control performance was improved by using temperature difference controllers instead of regular temperature control loops, which is why the authors recommend this system for practical application.

The control of an LOT-s-mDWC separating methanol, ethanol, propanol and butanol is investigated by Li et al. [96] based on Aspen Dynamics simulations. The LOT-s-mDWC is based on the simplified 2–2–4a configuration (Fig. 7-(IV)) and thus all vapor splits are completely eliminated. Both a CC– as well as a TEMPC-system were investigated for throughput and feed composition disturbances of ± 15 %. With the CC-system, the compositions were controlled effectively with small remaining offsets in the product composition of < 0.5 %. However, since the direct control of the compositions was relatively slow, the TEMPC-system was implemented as a comparison. Here again, effective control is observed with small remaining composition offsets and improved dynamic performance, showing that the LOT-s-mDWC can be controlled with relatively simple means like a decentralized control system.

To conclude this subsection, various researchers have investigated the control of LOT-sequences with a focus on the LOT-FC and the LOT-Kaibel-FC and first investigations on LOT-mDWC control. Different control schemes were proposed in varying degrees of complexity including composition- as well as- temperature control loops and regular control loops as well as ratio controllers and difference controllers. These investigations demonstrate that based on the dynamic simulation models LOT-sequences can be effectively controlled with decentralized control schemes, capable of handling throughput and composition disturbances of up to ± 20 %. Enhanced dynamic performance is typically achieved with more sophisticated controller architectures, such as those integrating feedforward or difference controllers. However, it should be noted that the outcome of dynamic control studies are contingent upon various factors, including the specific sequence dynamics, control system architecture, controller tuning, and the nature of disturbances under investigation. As such, the results obtained here are by no means generally transferrable. However, the successful application of diverse control schemes underscores the expectation of an easy controllability of LOT-sequences. This was especially substantiated by Kong et al. [92], who not only setup a control system for the LOT–Kaibel–FC but also compared it directly to the simple 3-DS and found that both sequences are comparable in terms of controllability. Nevertheless, competitive evaluations of the dynamic control of LOT- and conventional TC-sequences has not been investigated in detail and most importantly all of the performed control studies so far are theoretical model-based studies, without any experimental validation.

5. Application in advanced distillation processes

The characteristics and advantages of the LOT-concept have been investigated beyond simple sequences for the separation of zeotropic mixtures, in combination with other intensification strategies. Especially the individual pressure setting is advantageous for several advanced process intensification techniques, which are further discussed in this section. So far different concepts of heat-integrated LOT-sequences have been studied (cf. Section 5.1). Also, the combination of reactive distillation and the LOT-sequence has been investigated (cf. Section 5.2). Furthermore, especially in the field of extractive distillation, the LOT-SR sequence has found great appeal in a number of publications, which are discussed in Section 5.3.

5.1. Heat-Integrated concepts

A distillation column can be conceptualized as a heat engine that transforms the high temperature heat duty of the reboiler into separation work performed at the temperature level of the condenser such that excess heat is provided by the distillation column at the temperature level of the condenser [108]. This excess heat can be utilized in a distillation sequence exploiting the pressure dependence of boiling temperatures, either by direct heat integration, requiring modification of the operating pressure of one of the columns, or by means of heat-pump assisted distillation. Both of these concepts have been investigated for LOT-sequences.

Direct heat integration (HI) of distillation sequences is an established concept in the chemical industry [109] and requires either a reduction or an increase of the operating pressure in one of the adjacent columns, such that the condensation of the vapor at the top of one column is performed at a sufficiently high temperature to enable the evaporation

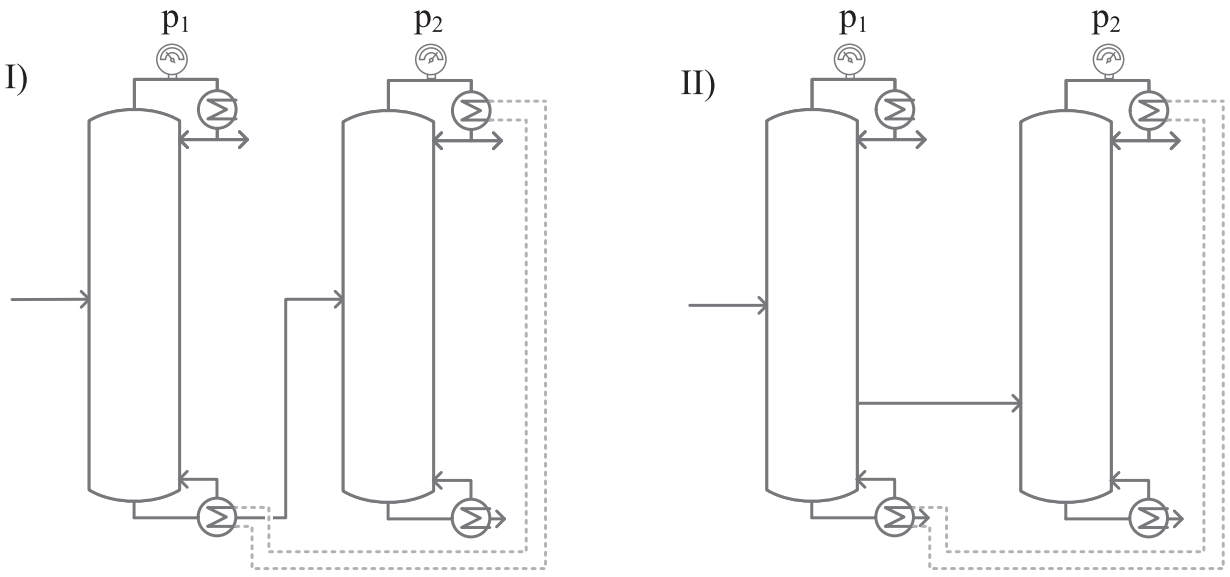

Fig. 11. Illustration of I) possible heat integration for a direct sequence and II) a liquid-only-transfer-side-rectifier HI-LOT-SR.

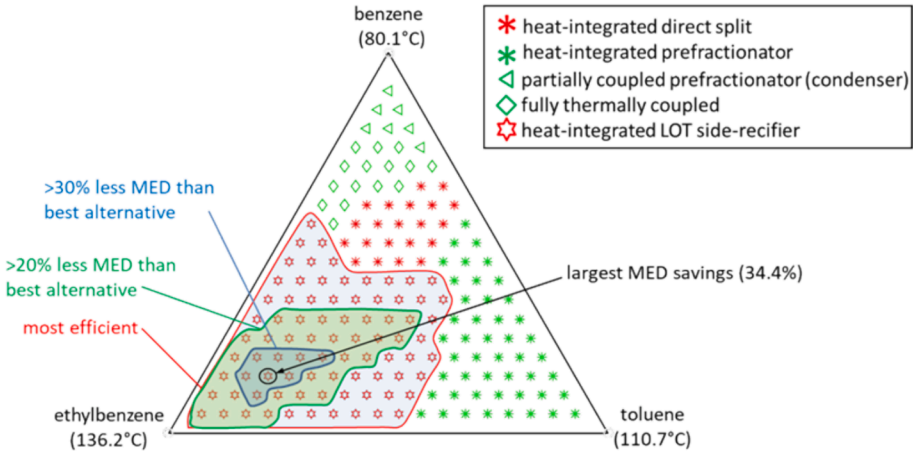

Fig. 12. Illustration of favorable process configurations for the separation of a benzene-toluene-ethylbenzene mixture in terms of minimum energy demand (MED) for different feed compositions (symbols indicate favorable process configuration at the specific feed composition). Reproduced from [81] with permission of Elsevier.

at the bottom of the other column. This is sketched exemplarily for the direct sequence in Fig. 11-(I). Here, the pressure in the first column is smaller than the pressure in the second column $p_1 < p_2$. However, a combination of direct heat integration with thermally coupled distillation is usually infeasible, since both columns are hydrodynamically linked through the bi-directional vapor–liquid transfer. In the LOT-sequence, this limitation can be overcome and direct heat integration can be combined with thermal coupling, as exemplarily illustrated for the LOT-SR in Fig. 11-(II). For this configuration either the pressure in the second column can be elevated or the pressure in the first column can be decreased. As such, the boiling temperature difference between the middle boiling component $T^B_{Mid}(p_2)$ and the high boiling component $T^B_{High}(p_1)$ can be manipulated so that $T^B_{Mid}(p_2) = T^B_{High}(p_1) + \Delta T$. Since the required heat exchanger area is usually proportional to the mean temperature difference and heat needs to be supplied to the second column above the temperature of the high boiling component at the higher pressure $T^B_{High}(p_2)$, the temperature difference ΔT is a tradeoff and usually around a value of approximately 10 K. Agrawal initially patented this concept in 2000 [110,111] and further published a study that evaluated the possible improvements with respect to uncoupled and thermally coupled sequences, based on the assumption of constant relative volatilities [112]. He concluded that the heat-integrated LOT-sequences required substantially lower heat duties than heat-integrated direct or indirect sequences. Compared to thermally coupled sequences the heat-integrated LOT-sequences enabled up to 50 % energy reduction compared to the DWC, especially for systems with quite dissimilar relative volatilities between the light and medium boiling component and the medium and high boiling component.

A further study of the HI-LOT-sequences based on more rigorous models was performed by Skiborowski [81], who conducted a shortcut based screening of all simple and TC-sequences in comparison to the HI-LOT-SR to evaluate the possible energy savings for the separation of a ternary mixture of benzene, toluene and ethylbenzene at varying feed compositions, making use of the rectification body method [77,80]. This scouting study showed that the HI-LOT-SR provides significant energy savings of 30 % and more compared to the DWC for feed compositions that are lean in the intermediate boiling toluene and rich in high-boiling ethylbenzene, as illustrated in Fig. 12.

An additional economic optimization based on a superstructure formulation for the HI-LOT-SR and the DWC [25] for feed composition that resulted in the highest energy savings did confirm the shortcut

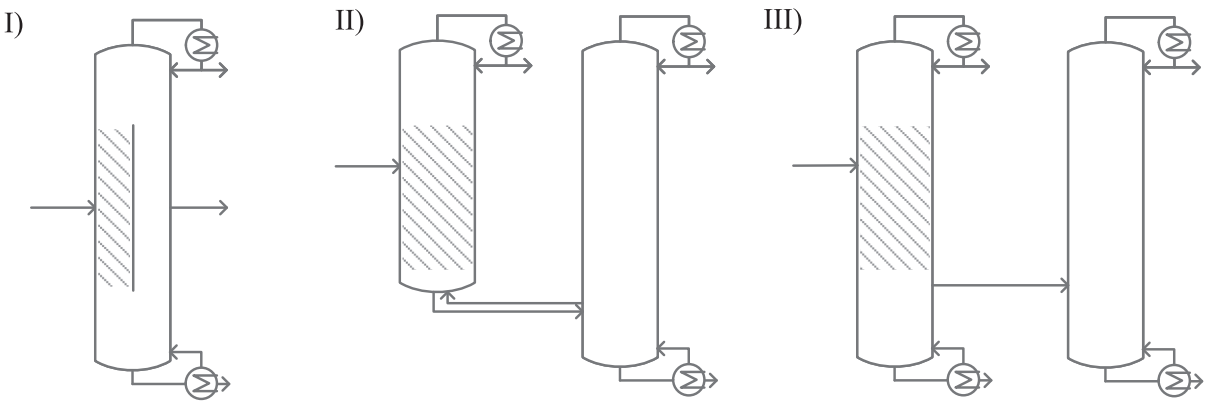

Fig. 13. Illustration of I) Regular reactive dividing wall column (RDWC), II) thermally coupled reactive side rectifier column (R-TC-SR) and III) LOT-version of a thermally coupled reactive side rectifier column (R–LOT–SR).

results, but also indicated that depending on the economic scenario the DWC may still be economically favorable for a grassroot design, given the reduced CAPEX. The shortcut screening studies were further extended in the work of Adami et al. [82] evaluating the specific OPEX estimates and including the separation of hexanol, octanol and decanol in vacuum. Despite variations in the extent of the energy savings and the range of the feed compositions the study confirmed the previous results for the vacuum separation case study as well. In terms of operational costs, the advantage of the HI-LOT-SR over the DWC strongly depends on the available heating utilities since higher-pressure steam might be necessary for the heat integrated sequences, driving up the cost of the HI-LOT-sequences.

Another investigation of an LOT-sequence with direct heat integration was conducted by Zhang et al. [113] in their study on the purification of a bioethanol fermentation broth which is approximated by the separation of carbon dioxide, water and ethanol. They use a sequential iterative design strategy to design several sequences based on Aspen Plus's Radfrac simulations and compare an LOT-SR, a configuration with a vapor-only-transfer as well as an HI-LOT-SR and more complex configurations consisting of three columns with both a vapor and a liquid side stream that are transferred two separate columns. The authors find that while the energy requirement of the HI-LOT-SR is smaller than that of the LOT-SR, the TAC of the HI-LOT-SR is 11 % higher than that of the simple LOT–SR, which is due to the significantly higher investment cost of the HI-LOT-SR. Here again, it becomes apparent that while the heat integrated process requires less energy, it might not be the most economical within a grassroot design procedure. However, it should be noted that it is not discussed specifically, why the difference in investment for the LOT-SR and the HI-LOT-SR is so substantial and no specific correlation is provided on the contribution of the heat integration to CAPEX. So far, no retrofit designs for HI-LOT-sequences have been discussed in the literature. Yet, given the high energy saving potential of HI-LOT-sequences in combination with higher investment costs for a grassroot design, this is a very promising concept that should receive further attention regarding both process design and control.

The other popular energy heat-integration concept analyzed in the context of LOT-sequences is vapor recompression (VR). In contrast to direct heat integration, VR can also be used with regular TC-sequences [114], alleviating the unique selling point of LOT-sequences in this context. However, LOT-sequences still offer the remaining advantages like easier operation and retrofitability, which is why VR-LOT is still a promising concept worth investigating. Duanmu and Sorensen [55] proposed different VR schemes for LOT–FC–DWCs and show that approximately 41 % of OPEX or 18 % of TAC can be saved compared to the conventional DWC for a BTX-separation. Their study included LOT–FC–DWCs with combined or individual condensers and reboilers and top-to-bottom vapor recompression connections. They utilized a combined stochastic-deterministic optimization including particle swarm optimization for the optimal design of the VR-LOT-DWCs based on gProms ProcessBuilder simulations. Song et al. [115] expanded this concept to a VR–LOT–Kaibel–DWC with top-to-bottom and intermediate vapor recompression and conduct and exergetic analysis as well, which is of particular interest, given the different forms of energy. They utilize a sequential iterative design based on Aspen Plus' Radfrac and conclude that for a benzene/toluene/o-xylene/1,3,5-trimethylbenzene mixture, using an LOT-Kaibel-DWC can save 27 % of energy when compared to the uncoupled direct sequence consisting of three columns. Introducing a top-to-bottom VR saves an additional 3,6% of energy. Most interestingly, introducing an intermediate VR to the LOT–FC–DWC increases the thermodynamic efficiency from less than 10 % for the uncoupled direct sequence to approx. 15 %. This configuration is also identified as the least expensive regarding the TAC estimates.

5.2. Reactive distillation

The combination of reactive distillation and thermal coupling, e.g. in reactive dividing wall columns (RDWC) as shown in Fig. 13-(I) is an established concept in academic research [33]. However, despite reported energy saving potentials of 15–75 % [33] and experimental studies on pilot plants that prove feasible operability [116,117], the RDWC has not yet been industrially applied due to its complexity and limited process window and flexibility. Due to this, the RDWC is an interesting target for simplification by an LOT-adaption. Ge et al. [118] investigated an R–TC–SR (Fig. 13-(II)) and transformed it to an R–LOT–SR (Fig. 13-(III)). A genetic algorithm was used to calculate optimal designs. Nearly equivalent energy consumption for the R-LOT-SR and the regular R–TC-SR were shown, substantiating the thermodynamic equivalence even with an integrated reaction. Apart from possible operational advantages, individual pressure can be used to alter the operating windows and directly influence reaction conditions. The study by Ge et al. [118] illustrates this for formic acid production based on methyl formate hydrolysis. While the TAC of the R-TC-SR are higher than that of the uncoupled reactive distillation sequence that allows for pressure variation, the R-LOT-SR for which pressure variations are also feasible, enables a TAC reduction of 6.6 % in comparison to the uncoupled alternative. Furthermore, dynamic studies with a decentralized and centralized control systems were conducted, whereas a centralized model predicative controller proved to be well-suited to control the R-LOT-SR.

5.3. Extractive distillation

Extractive distillation is used to separate azeotropic mixtures or close-boiling nonideal mixtures that are challenging to separate by

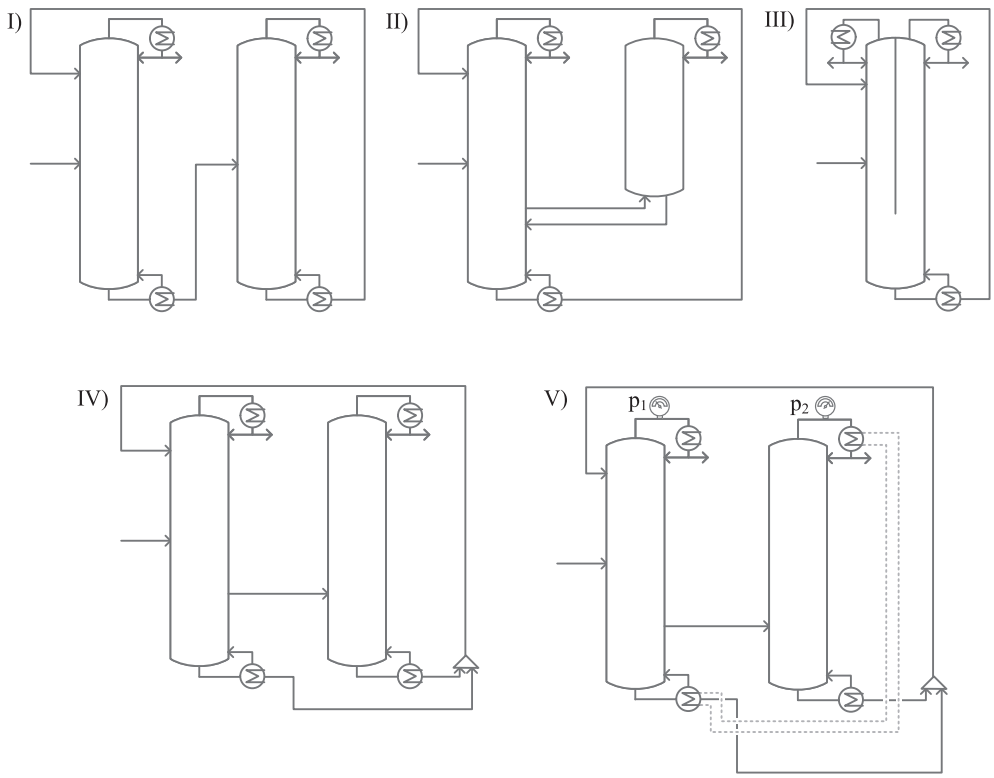

Fig. 14. Sketch of I) a regular extractive distillation sequence, II) an extractive side rectifier sequence E-TC-SR, III) an extractive dividing wall column E-DCW-SR, IV) an LOT-E-SR and V) an HI-LOT-E-SR.

introducing a solvent that manipulates the relative volatility of the components to be separated. The solvent is subsequently recovered in a second column and recycled to the first column. A sketch of this is shown in Fig. 14-(I), purge and make up streams are omitted in the graph for better clarity. This process can be integrated into a thermally coupled sequence, e.g. an extractive side rectifier (E-TC-SR; Fig. 14-(II)) or an extractive dividing wall column (E-DWC; Fig. 14-(III)), which reportedly enables energy savings between 10 %–30 % in comparison to an uncoupled extractive distillation sequence [119,120] and is industrially employed [30]. However, E-DWCs are not necessarily economically attractive, as e.g. demonstrated by Wu et al. [121] and Waltermann et al. [122]. Furthermore, it is shown that the control performance of the E-DWC is subpar, when the vapor split is not utilized as a manipulated variable [44,121]. Czarnecki et al. [32] just recently published a review on E-DWC, including a comprehensive overview on the different studies and more than 30 azeotropic systems that have been investigated. They also address the complexity of the vapor split and the opportunity to use LOT, however mistakenly conclude that this has not yet been studied. This is not surprising, considering that in the field of extractive distillation, the term "energy-efficient side-stream extractive distillation" prevails over the terminology "Liquid-Only-Transfer". Yet, the LOT-concept has found great appeal in the field of extractive distillation with, to the best of our knowledge, Tututi-Avila et al. [57] being the first to analyze an LOT-version of the E–TC–SR in 2017 (Fig. 14-(IV). They confirm that their configuration was motivated by the work of Agrawal [50]. In this study, they investigated the saving potential for three case studies, covering the separation of ethanol and water assisted by ethylene glycol, heptane and toluene assisted by aniline and acetone and methanol assisted by water. For the acetone-methanol–water system, a heat integrated version of the LOT-E-SR is considered as well (HI-LOT-E-SR, Fig. 14-(V)). TAC-optimal designs of the E–TC-SR, the LOT-E-SR and as a reference the regular extractive distillation sequence are obtained by means of a genetic algorithm implemented in MATLAB linked to Aspen Plus simulations with Radfrac models. For all three case studies similar saving potentials with 13–14 % of the total heat duty and 12–13 % in TAC were reported when comparing the LOT-E-SR to the regular extractive distillation process. In the case of the ethanol–water system, the authors highlight the possible retrofit of the LOT-E-SR, since it requires the same number of equilibrium stages as the regular extractive distillation process. Taking into account further heat integration, a heat duty reduction of 31 % and a TAC reduction of 29 % is possible for the regular process for the acetone–methanol separation. This is even surpassed for the HI-LOT-E-SR with a saving potential of 39 % heat duty and 36 % TAC compared to the regular extractive distillation process.

Considering these substantial saving potentials, it is not surprising that the LOT-versions of extractive distillation processes have found great appeal in further publications referring to them almost exclusively as energy-efficient side-stream extractive distillation. With more than 20 publications on extractive LOT-sequences most research papers have been published from research groups in China. A summary of the publications on LOT-versions of extractive distillation is provided in Table 2, providing information on the studied substance system, the specific LOT-process and design methodologies, following the categories reported in Section 3.1, as well as dynamic control studies, as discussed in Section 4.2.

With regards to process design, most of the publications utilize a sequential iterative design strategy, while some apply genetic algorithms like NSGA-II [123] or a multi-objective genetic algorithm [124]. Apart from that, particle swarm optimization [125] and differential evolution [126] have been studied and a number of researchers adapted the simulated annealing algorithm for optimizing LOT-designs [127–129].

In terms of control studies, all of the mentioned publications investigated disturbances in a range of 5–20 % both in throughput as well as in feed composition. The majority of researches implemented decentralized PI-control loop schemes, both with pure TEMPC-systems as well as hybrid temperature-composition control systems. All of these decentralized control systems included ratio controllers on the feed.

Table 2
Summary of publications in the field of extractive LOT-processes (Note that all of the mentioned publications in this table either used Aspen Plus for steady state calculations and/or Aspen Dynamics for dynamic simulations, hence information on software and model are omitted in this table; All sequences from this table that are sketched in the Supporting Information can be found in SI-7).

Substance System with Solvent S	LOT-Processes	Design	Control Strategy		
			Disturbances	Control Scheme	
Acetone Methanol S: Water	LOT-E-SR	Design as in Tututi-Avila et al. [57]	10–20 % disturbance in throughput and feed composition	Scheme with temperature and ratio control loops; Hybrid schemes with temperature-, composition-temperature cascade- and ratio control loops	[131]
Acetone Methanol S: Water	LOT-E-SR; HI-LOT-E-SR	Design as in Tututi-Avila et al. [57]	20 % disturbance in throughput and feed composition for LOT-E-SR 10 % disturbance in throughput and feed composition for HI-LOT-E-SR	Schemes with temperature and ratio control loops; Hybrid schemes with temperature-, composition- and ratio control loops	[132]
Ethylacetate Ethanol S: Dimethylsulfoxide (DMSO)	LOT-E-SR	Sequential iterative design	20 % disturbance in throughput and feed composition	Scheme with temperature and ratio control loops; Hybrid scheme with temperature-, composition- and ratio control loops; Hybrid schemes with temperature-, composition-temperature cascade- and ratio control loops	[133]
Ethylacetate Ethanol S: DMSO	LOT-E-SR	NSGA-II	10 % disturbance in throughput and feed composition	Scheme with temperature and ratio control loops; Hybrid schemes with temperature-, composition- and ratio control loops	[123]
Methanol Toluene S: Triethylamin	LOT-E-SR; LOT-E-SS	Genetic algorithm	–	–	[53]
Methanol Toluene S: Triethylamin	LOT-E-SR	Design as in Wang et al. [53]	10 % disturbance in throughput 20 % disturbance in feed composition	Scheme with temperature and ratio control loops; Hybrid schemes with temperature-, composition- and ratio control loops	[134]
Propylenoxid Methanol S: Water	LOT-E-SR	Sequential iterative design	10 % disturbance in throughput and feed composition	Scheme with temperature and ratio control loops; Hybrid schemes with temperature-, composition- and ratio control loops	[135]
Isopropanol Water S: Ethylenglycol (EG)	LOT-E-SR	NSGA-II	–	–	[136]
Acetone n-Heptane S: Xylene	LOT-E-SR	Sequential iterative design	–	–	[54]
Dichlormethane Methanol S: Dimethylformamid	LOT-E-SR	Retrofit simulation based on E-DS	10 % disturbance in throughput 5 % disturbance in feed composition	Schemes with temperature and ratio control loops	[103]
Chloroform N-hexane S: N-Methylpyrrolidone	LOT-E-SR	Sequential iterative design	Control study only for E-TC-SR, not for LOT-E-SR	Control study only for E-TC-SR, not for LOT-E-SR	[137]
Ethylenglycol 1,2-Butanediol S: Eugenol	LOT-E-SR	Sequential iterative design	–	–	[138]
Acetonitrile Benzene Methanol S: Chlorobenzene (CB)	Double LOT-E-SR* with connection via the first and second column; 3–LOT–E–SR*	Sequential iterative design	–	–	[139]
Acetonitrile Benzene Methanol S: CB	3–LOT–E–SR	Sequential iterative design	5 % disturbance in throughput 10 % disturbance in feed composition	Hybrid scheme with temperature-, composition- and ratio control loops	[140]
Acetonitrile Benzene Methanol S: CB	3–LOT–E–SR	Design as in Wang et al. [139]	10 % disturbance in throughput and feed composition	Scheme with temperature and ratio control loops	[141]
Acetonitrile Benzene Methanol S: CB	3–LOT–E–SR	Design as in Wang et al. [139]	10 % disturbance in throughput and feed composition	Scheme with temperature and ratio control loops; Scheme with temperature difference and ratio control loops	[142]
Acetonitril Isopropanol Water S: Ethylenglycol (EG)	LOT-E-SR with subsequent column in DS; DS with subsequent LOT–E–SR; 3–LOT–E–SR including heat pumps and heat integration	Genetic algorithm	–	–	[143]

(continued on next page)

Table 2 (*continued*)

Substance System with Solvent S	LOT-Processes	Design	Control Strategy		
			Disturbances	Control Scheme	
Benzene Isopropanaol Water S: EG	LOT-E-SR with subsequent column in DS; DS with subsequent LOT–E–SR; 3–LOT–E–SR	Simulated Annealing Algorithm	–	–	[127]
Benzene Isopropanaol Water S: EG	3–LOT–E–SR	Design as in Cui et al. [127]	10 % disturbance in throughput 20 % disturbance in feed composition	Scheme with temperature and ratio controllers	[144]
Benzene Isopropanaol Water S: EG	3–LOT–E–SR	Design as in Cui et al. [127]	20 % disturbance in throughput 10–20 % disturbance in feed composition	Scheme with temperature and ratio control loops; Hybrid scheme with temperature-, composition-, composition-temperature cascade- and ratio control loops	[145]
Water Acetic Acid Cyclohexane S: Cyclohexanone	LOT-SR with subsequent column in DS 3-LOT-E-SR	Sequential iterative design	20 % disturbance in throughput 20 % disturbance in feed composition	Scheme with temperature and ratio controllers; Model predictive controller	[130]
Benzene Cyclohexane Cyclohexene S: Dimethylacetamide	3-LOT-E-SR and variations	Differential Evolution	–	–	[126]
Isopropanol Ethylacetat Water S: EG	LOT-E-SR with reactive section	Particle Swarm Optimization	–	–	[125]
Methylethylketon Isopropanol Water S: EG	3–LOT–E–SR	Sequential iterative design	–	–	[146]
Toluene Methanol Water S: Glycerol	LOT-E-SR with decanter	Multi Objective Genetic Algorithm	–	–	[124]
Acetone Methanol Butanone Tert butanol S: CB	4-LOT-E-SR*	Simulated Annealing Algorithm	10 % disturbance in throughput and composition	Scheme with temperature and ratio controllers; Hybrid scheme with temperature-, composition- and ratio control loops	[128]
Acetone Methanol Butanone Tert butanol S: CB	4-LOT-E-SR and variations with DS	Simulated Annealing Algorithm	–	–	[129]

Furthermore, a model predictive controller was implemented and tested successfully by Liu et al. [130].

Finally, the integration of a reactive zone into the extractive distillation unit was discussed by Yang et al. [125] for the recovery of isopropanol and ethyl acetate from wastewater by adding ethylene oxide to the reactive column. Together with water, this builds ethylenglycol, which is used as the entrainer. This study is conducted in an LOT-E-SR with a reactive zone integrated into the first column.

6. Summary and conclusion

The current review provides an overview of the research conducted on LOT-sequences, which despite of a significantly lower coverage than thermal coupling and dividing wall columns, have received quite a broad interest to date. In a number of publications dedicated to the synthesis of LOT-sequences it was shown, that the simple LOT-concept can be applied to arbitrarily complex thermally coupled systems, which was illustrated up to quinary separations. In terms of design, both shortcut methods as well as a number of design methods based on rigorous models have been used for the evaluation and optimization of the energy demand and the total annualized costs. For simplicity an equivalence-based design approach can be pursued, which essentially duplicates and rearranges column segments from a thermally coupled sequence. This is a simple and quick method, however, in some cases yields non-optimal energy demands. Various optimization strategies for grassroot design have been applied to LOT-sequences of varying degrees of complexity. Most of them apply sequential iterative or single/multi-objective stochastic algorithms linked to a tailored process model in a commercial flowsheet simulator. These methods may require multiple runs to validate the quality of the solution due to the stochastic nature of the algorithms. Direct equation-based optimization of LOT-processes making use of gradient based solvers has so far received limited attention. Nevertheless, it can be concluded that several established and tested design strategies are available for grassroot design of LOT-sequences. Concerning controllability, theoretical control properties of LOT-sequences like minimal singular values and condition numbers have been calculated. So far, this has been conducted only for LOT-SS and LOT-SR, not for the fully coupled LOT–FC–DWC or more complex sequences. Furthermore, a number of dynamic control studies with control systems based on temperature and composition control have been studied and successfully demonstrated on different kind of LOT-sequences. Additionally, the LOT-concept has been applied to further integrated processes considering heat integration, reactive distillation and especially extractive distillation. It was shown, that in all of these processes, the LOT-concept provided certain advantages, mainly due to individual pressure setting. Other azeotropic distillation processes such as pressure swing or heteroazeotropic distillation have not been investigate so far.

Evidently, the concept has been embraced in academic research and important theoretical investigations have been conducted. However, up

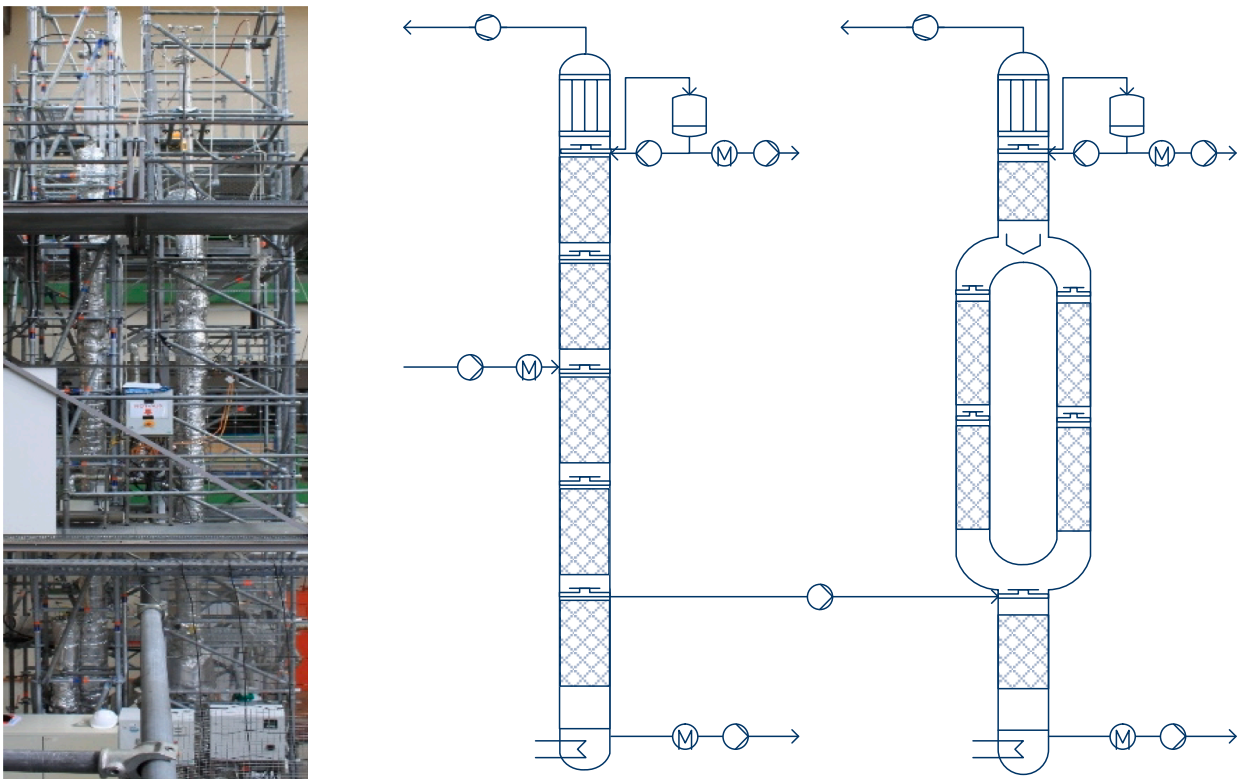

Fig. 15. Photography of the multipurpose distillation pilot plant and simplified sketch of the columns.

to date no dedicated industrial implementation or even experimental studies on laboratory scale of an LOT-sequences have been reported so far. We ascribe this to a number of crucial research questions which have not yet been answered. In order to advance LOT-research and implementations, we believe that the following topics should receive immediate attention:

(I) Retrofit Potential

As shown in Section 3, a number of established grassroot design strategies have been applied successfully to different forms of LOT-sequences. Yet, retrofit studies are scarce. Considering that for an exemplary case study [102], the amortization of a retrofit investment for an LOT-SR was under 2 years with OPEX savings of up to 20 %, this topic proves to be very promising for industrial implementation. Due to this, detailed retrofit studies for a wider range of different LOT-applications, especially considering the fully coupled LOT–FC–DWC and additional heat integration should be conducted.

(II) Flexibility of LOT-Sequences

Due to the structure of LOT-sequences, they have one more manipulated variable when compared to their TC-counterparts. Based on this, it can be expected, that a manipulation of the operating point can be conducted more directly. Especially compared to a dividing wall column, where the vapor split is essentially defined at the design stage of the column, the LOT-sequence should be more flexible. While Ramapriya et al. [37] showed, that the vapor split range in which an optimal energy demand is realizable can be quite narrow, no research group has conducted comprehensive studies on the flexibility of LOT-sequences.

(III) Thermodynamic efficiency considerations

The majority of studies focuses on minimal energy demands and uses it as a reference value. Even though the energy demand is a very important value for the assessment of a sequence, crucial information like the energy form or temperature level of required and rejected heat is neglected. In order to regard this information, the thermodynamic efficiency of a process should be assessed. For the purpose of a complete evaluation, this is especially important when comparing different intensified approaches like e.g. heat-integrated LOT and heat-pump-assisted distillation.

(IV) Advanced process control

It has been shown, that LOT-sequences can be operated with a structure of simple PI-loops (Section 4). While simple, decentralized structures lay the groundwork for industrial operation, more advanced process control schemes offer certain advantages. Namely model predictive controllers can be considered state of the art, especially in the field of distillation and would offer the opportunity of energy optimal control trajectories, tying into the flexibility of LOT-sequences (Point III).

(V) Experimental Validation

So far, all of the mentioned analyses are exclusively model-based, relying on equilibrium-stage models for steady state and dynamic simulations. However, a critical review of all of the advantages and characteristics of LOT-sequences must still be performed on a practical level, in order to experimentally validate the concept and conclusively pave the way for an industrial implementation.

In order to effectively address this last point and fill this important gap, our research group has recently built a multipurpose distillation sequence that allows the study of simple sequences, DWC and LOT-sequences. The respective setup is illustrated in Fig. 15 indicating the currently employed configuration in which the regular distillation column and the dividing wall column, which is currently operated as an individual column, are connected via a single side stream, employing the LOT-SR configuration. Both columns are stainless steel columns with a

height of ~ 12 m a diameter of DN50/DN65 and are equipped with Montz B1-500 structured packings. A publication on the specific design, modeling and start-up is currently in preparation.

The conceptual and practical benefits and limitations of the LOT-concept should be analyzed comprehensively, delineating its potential and applicability. By addressing these five crucial research topics, the path for a dedicated industrial implementation can be paved. Given the simplicity of the LOT-concept combined with possibly substantial energy savings, it has the potential to significantly impact the chemical industry, much like the closely related dividing wall column. Moreover, by demonstrating its unique features in terms of retrofitting, flexibility and further integration opportunities, the LOT-concept could become a versatile and highly efficient option for a wide range of separation processes, driving further innovation and sustainability in industrial applications.

CRediT authorship contribution statement

Anna Sophia Horsch: Writing – review & editing, Writing – original draft, Visualization, Conceptualization. **Mirko Skiborowski:** Writing – review & editing, Supervision, Project administration, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used ChatGPT-3.5 in order to improve readability and language. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.128762.

*Due to the vast variety of sequences discussed in this contribution, it is not expedient to include a sketch of all sequences in the main text. All sequences marked with * are sketched in the supplementary information.

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