

# REACTIVE DISTILLATION FOR MULTIPLE-REACTION SYSTEMS: OPTIMISATION STUDY USING AN EVOLUTIONARY ALGORITHM

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Reactive distillation (RD) has already demonstrated its potential to significantly increase reactant conversion and the purity of the target product. Our work focuses on the application of RD to reaction systems that feature more than one main reaction. In such multiple-reaction systems, the application of RD would enhance not only the reactant conversion but also the selectivity of the target product. The potential of RD to improve the product selectivity of multiple-reaction systems has not yet been fully exploited because of a shortage of available comprehensive experimental and theoretical studies. In the present article, we want to theoretically identify the full potential of RD technology in multiple-reaction systems by performing a detailed optimisation study. An evolutionary algorithm was applied and the obtained results were compared with those of a conventional stirred tank reactor to quantify the potential of RD to improve the target product selectivity of multiple-reaction systems. The consecutive transesterification of dimethyl carbonate with ethanol to form ethyl methyl carbonate and diethyl carbonate was used as a case study.

**Keywords:** nonequilibrium-stage model, Pareto-front, multi-objective optimisation, diethyl carbonate, ethyl methyl carbonate

## 1. INTRODUCTION

The combination of chemical reaction and thermodynamic separation inside a single unit represents one of the most promising methods of implementing process intensification (Schmidt-Traub and Górak, 2006; Stankiewicz, 2003). Compared to conventional reaction-separation sequences, such so-called integrated reactive separation processes offer the potential for large savings of capital, energy, and materials (Górak and Stankiewicz, 2011; van Gerven and Stankiewicz, 2009). One of the most important industrial applications of the integrated reactive-separation concept is reactive distillation (RD), in which reaction and distillation occur at the same time and in the same location (Schoenmakers and Bessling, 2003). RD allows for higher reactant conversion, product selectivity and energy savings with favourable investment and operating costs. However, in contrast to the above-mentioned advantages, there are several constraints that limit the successful application of RD, such as complex design, difficult scale-up and advanced process control (Schoenmakers and Bessling, 2003; Sundmacher and Hoffmann, 1996). Nevertheless, RD has been industrially applied for certain types of chemical-equilibrium limited reactions, the most important being esterifications (Agreda et al., 1990;

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Keller et al., 2011b; Schmitt et al., 2004), transesterifications (Steinigeweg et al., 2004) and etherifications (González-Ruggerio et al., 2012; Sundmacher and Hoffmann, 1996).

The majority of papers published on RD investigate relatively simple reaction systems that are composed of a single main reaction. For these single-reaction systems, RD has already demonstrated its potential to overcome conversion limitations set by chemical equilibrium. In contrast, there are only few publications that cover more complex reaction systems featuring more than one main reaction. In such multiple-reaction systems, RD can be applied to enhance reactant conversion as well as the selectivity of the target product, regardless of whether it is formed as an intermediate product or at the end of several consecutive reactions. In this context, Thotla and Mahajani (2009) proposed to design guidelines at the conceptual design level using various configurations of RD columns to improve selectivity in multiple-reaction systems. In addition, experimental studies have recently been performed by several researchers. Thotla et al. (2007) experimentally studied the aldol condensation of acetone to form diacetone alcohol. The target product, diacetone alcohol, is formed as an intermediate product and can dehydrate in a subsequent reaction to form mesityl oxide and water. The authors applied RD to continuously remove diacetone alcohol from the reaction section, thereby suppressing the formation of mesityl oxide. However, the dehydration of diacetone alcohol is very fast compared to the aldol condensation of acetone and, therefore, diacetone alcohol selectivities of only 34.6% were achieved for acetone conversions near 100%. Talwalkar et al. (2007) experimentally studied the heterogeneously catalysed dimerisation of *iso*-butene to form the target product *iso*-octane. The authors experimentally demonstrated that RD can be effectively used to improve the selectivity of *iso*-butene, thereby suppressing the formation of trimers and tetramers. Selectivity towards *iso*-octane of approximately 90 % was achieved. The authors developed a nonequilibrium-stage model that demonstrated sufficient agreement with the experimental data. However, a detailed process analysis and optimisation study to further improve the product selectivity were not presented.

RD can also be used to effectively increase the selectivity of a target product formed at the end of several consecutive reactions. For example, Suman et al. (2009) studied the esterification of ethylene glycol with acetic acid. The chemical system consists of two consecutive reactions whereby the target product ethylene glycol diacetate is formed through a second consecutive reaction. The authors experimentally and theoretically demonstrated that the use of RD significantly increases the selectivity towards ethylene glycol diacetate. Hasabnis and Mahajani (2010) reported the successful use of semibatch RD in the synthesis of triacetin to enhance selectivity. They stated that a selectivity towards triacetin of 100 % can be obtained that is much greater than that offered by any conventional reactor with the same reactant molar ratio. Orjuela et al. (2011) performed experiments using a pilot-scale RD column to study the esterification of succinic acid with ethanol. The chemical system consists of two consecutive reactions, and the target product diethyl succinate is formed in the second reaction. According to the authors, a succinic acid conversion of 100 % and a diethyl succinate selectivity of 98 % were experimentally achieved. The experimental results were used to successfully validate the equilibrium-stage model provided by Aspen Plus. However, the authors did not present any optimisation studies using the validated model.

Another promising example is the reversible consecutive second-order transesterification of dimethyl carbonate (DMC) with ethanol to form ethyl methyl carbonate (EMC) and diethyl carbonate (DEC). There are already a few papers that explore the application of RD for that system. For example, Luo and Xiao (2001) demonstrated the feasibility of using RD to produce DEC with a selectivity exceeding 99.5 %. The authors simulated an RD column in which heterogeneous catalyst potassium carbonate was incorporated. However, no experimental investigation of RD process was reported to validate the applied process model. The work of Mueller and Kenig (2007) is also restricted to a purely theoretical analysis. They designed a reactive divided-wall column for the synthesis of DEC by applying the heterogeneous catalyst dipotassium carbonate coated on polyethylene glycol. The corresponding reaction kinetics were provided by Zielinska et al. (2006). The same reaction kinetics were also used by

Wei et al. (2011) to design, again through a purely theoretical approach, an RD column for the selective synthesis of DEC. However, it must be emphasised that Zielinska et al. (2006) reported some difficulties with the mechanical stability and the chemical resistance of the self-coated catalyst dipotassium carbonate. To our knowledge, no experimental results for the transesterification of DMC with EtOH in an RD column applying the catalyst dipotassium carbonate have yet been published in the literature, probably because of the aforementioned stability problems of the catalyst. Therefore, the theoretical investigations published so far for the transesterification of DMC with EtOH are based on process models that have not been validated against experimental data.

However, in one of our previously published articles, we have presented for the first time a comprehensive experimental study on that reaction system in a pilot-scale RD column (Keller et al., 2012). To enhance the reaction rate, sodium ethoxide was used as a homogeneous catalyst (Keller et al., 2011a). Moreover, we have already developed a nonequilibrium-stage model that has been successfully validated against the experimental data (Keller and Górak, 2013). Consequently, the present article uses, unlike the available publications in the literature, a successfully validated process model to theoretically investigate the transesterification of DMC with EtOH in an RD column.

The purpose of this article is to theoretically demonstrate that RD is able to overcome the limitation of target product selectivity in a multiple-reaction system, regardless of whether it is formed as an intermediate product or at the end of consecutive reactions. Both of these cases are treated in this article: EMC represents the intermediate target product, while DEC represents the final target product. For the analysis, an evolutionary algorithm is used to optimise decisive operating parameters of a pilot-scale RD column for maximum product selectivity, either towards EMC or DEC. These results are compared with those of a conventional stirred tank reactor to quantify the potential of the RD column to improve the target product selectivity of multiple-reaction systems.

## 2. CASE STUDY: TRANSESTERIFICATION OF DIMETHYL CARBONATE WITH ETHANOL

### 2.1. Reaction system

The chemical system investigated in this study is the consecutive transesterification of dimethyl carbonate (DMC) with ethanol to form ethyl methyl carbonate (EMC) and diethyl carbonate (DEC). Table 1 lists the nomenclature and the boiling points of the pure components at ambient pressure. The reaction that converts DMC to DEC is a two-step reaction, with the first step being the transesterification of DMC with EtOH to the intermediate EMC and the side-product MeOH (R1). The second step is the transesterification of EMC with EtOH to form DEC and MeOH (R2).

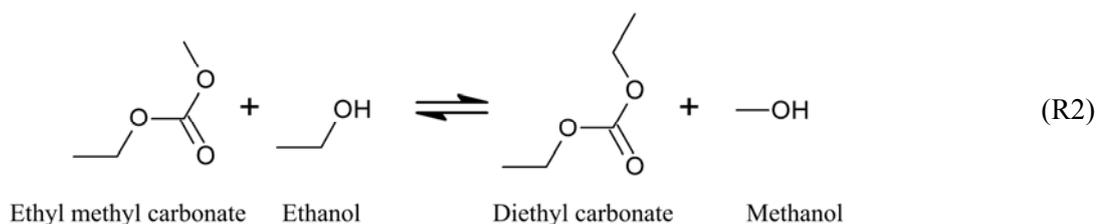
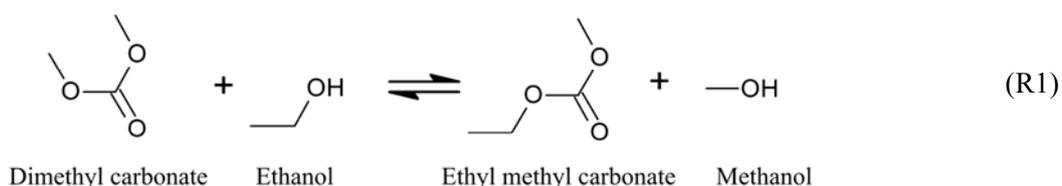


Table 1. Nomenclature and pure component boiling points (NIST, 2009) at  $P = 101.3$  kPa

Component	Abbreviation	Formula	CAS Number	$T_b$ (K)
Methanol	MeOH	CH <sub>4</sub> O	67-56-1	337.9
Ethanol	EtOH	C <sub>2</sub> H <sub>6</sub> O	64-17-5	351.4
Dimethyl carbonate	DMC	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	616-38-6	363.4
Ethyl methyl carbonate	EMC	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	623-53-0	380.8
Diethyl carbonate	DEC	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>	105-58-8	400

In our previous work, we found that sodium ethoxide is a suitable homogeneous catalyst to enhance the reaction rate (Keller et al., 2011a). The catalyst sodium ethoxide was used to experimentally determine the chemical equilibrium and reaction kinetics of the transesterification of DMC with EtOH. Over the investigated temperature range, the activity-based chemical equilibrium constant of the first reaction, the transesterification of DMC to EMC, ranged from 1.77 to 2.10, which was larger than the values of the second transesterification reaction (0.39–0.45), the transesterification of EMC to DEC. This indicates that the chemical equilibrium lies on the product side of the first transesterification reaction and on the reactant side of the second transesterification reaction.

Both EMC and DEC are industrially relevant products. The asymmetric carbonic ester EMC has been found to be a suitable co-solvent for incorporation into nonaqueous electrolytes to enhance the low-temperature performance of rechargeable alkali metal-ion batteries (Marshall et al., 2011; Okuno et al., 1996; Plichta and Behl, 2000; Takeuchi et al., 2010). DEC represents an attractive alternative for phosgene as an ethylation and carbonylation reagent in organic synthesis (Leino et al., 2010). Additionally, DEC can be used as a raw material for the manufacture of polycarbonates (Bolon and Hallgren, 1984). Like EMC, DEC is widely used as a co-solvent in alkali metal-ion batteries (Ding et al., 2001). Most importantly, DEC is considered to be one of the best alternatives for methyl *tert*-butyl ether (MTBE) as an oxygen-containing fuel additive (Dunn et al., 2002; Pacheco and Marshall, 1997).

## 2.2. Reactive distillation process

Because the transesterification of DMC with EtOH consists of two equilibrium-limited transesterification steps, the application of RD is an attractive intensification process to overcome conversion and selectivity limitations set by the chemical equilibrium.

The homogeneously catalysed transesterification of DMC with EtOH was previously investigated in a pilot-scale packed RD column and the experimental results can be found in the article of Keller et al. (Keller et al., 2012). The RD process which was experimentally studied is illustrated in Figure 1. Usually, the high-boiling component is fed to the RD column above the low-boiling component to establish a countercurrent flow and extensive contact between the reactants in the reactive zone. However, the homogeneous catalyst sodium ethoxide has a very low solubility in DMC, so the catalyst must be fed to the column together with the low-boiling reactant EtOH. Consequently, the reaction takes place in the whole column section below the feeding point of EtOH, which includes the reboiler. The feeding of the high-boiling component DMC above the low-boiling component EtOH would not be more beneficial because no reaction takes place between the feeding points of DMC and EtOH. Thus, both reactants enter the RD column at the same height. Assuming that full reactant conversion can be achieved, the target products EMC and/or DEC are removed at the bottom of the column, whereas the lowest-boiling component MeOH is obtained at the top of the column.

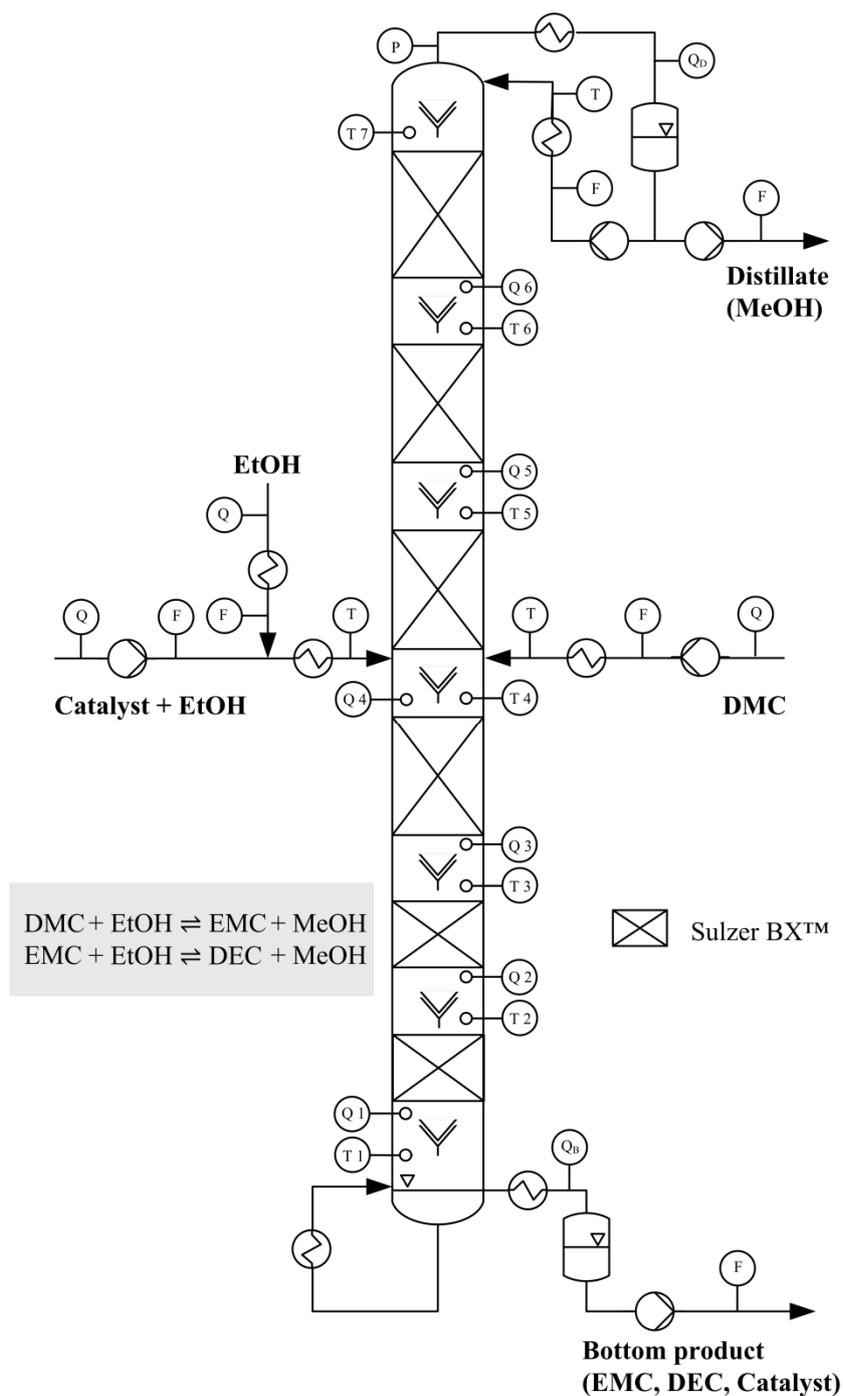


Fig. 1. Scheme of the pilot-scale RD column used by Keller et al. (2012) to investigate the homogeneously catalysed transesterification of DMC with EtOH

It must be stated that the optimisation studies performed in the present article are restricted solely to operational and not to structural parameters. Therefore, the same column configuration as used in the experimental study will be used for the optimisation studies. The experiments were performed in a pilot-scale RD column with a nominal diameter of 50 mm at ambient pressure. The column consisted of six packing sections, in which conventional structured Sulzer BX™ packing elements were incorporated. The total packing height was 5.4 m. Both reactants entered the RD column at the same packing height of 2.0 m. The homogeneous catalyst sodium ethoxide was fed to the RD column together with the low-boiling reactant EtOH. The relevant characteristics of the pilot-plant RD column are listed in Table 2.

Table 2. Characteristics of the pilot-scale RD column

Nominal diameter	50 mm
Total packing height	5.4 m
Total feed flow rate	4–6 kg/h
Feed location of	
DMC	2.0 m
EtOH	2.0 m
Catalyst	2.0 m
Stripping section	3.4 m (Sulzer BX™)
Rectifying section	2.0 m (Sulzer BX™)
Condenser type	Total
Reboiler type	Natural circulation reboiler
Process control system	Simatic™ PCS7
Operating pressure	Ambient

### 2.3. Modelling and simulation

RD is a multicomponent process that occurs in a multiphase fluid system. Consequently, multicomponent thermodynamic and diffusional coupling in the phases and at the interface are accompanied by complex hydrodynamics and chemical reactions (Kenig and Górak, 2007; Sundmacher and Kienle, 2003). An adequate description of RD processes therefore requires specially developed mathematical models that are capable of covering column hydrodynamics, mass and heat transfer resistances, and reaction kinetics simultaneously. Comprehensive reviews on the fundamentals of the different types of modelling approaches developed for RD processes are available in the literature (Kenig and Górak, 2007; Schmidt-Traub and Górak, 2006; Taylor and Krishna, 2000).

The models describing the RD processes can be primarily classified as either equilibrium-stage (EQ) or nonequilibrium-stage (NEQ) models. The EQ model assumes that both bulk phases are perfectly mixed and that the streams leaving the stage are in thermodynamic equilibrium. In contrast, the NEQ model takes into account the actual rates of multicomponent mass and heat transfer as well as process hydrodynamics (Noeres et al., 2003).

To simulate the homogeneously catalysed transesterification of DMC with EtOH in the pilot-scale RD column, a process model based on scientific work previously conducted at the Laboratory of Fluid Separations, TU Dortmund University, was applied. The model was originally developed by Górak et al. (2001) and was successfully used for the simulation of different RD processes (Hoffmann et al., 2004; Kenig et al., 2001; Kloeker et al., 2005). We have recently published an article, in which the model validation for the homogeneously catalysed transesterification of DMC with EtOH is comprehensively described (Keller and Górak, 2013). In this model, the mass and heat transfer across the vapour-liquid interface was described using the two-film theory (Lewis and Whitman, 1924). The multi-component diffusion in the films was modelled by the effective-diffusivity approach (Burghardt et al., 1983) and the Chilton-Colburn analogy (Chilton and Colburn, 1935) was applied for the calculation of the heat transfer rates. The hydrodynamics of the column internals were considered by the application of packing specific correlations (Bravo et al., 1985; Rocha et al., 1993). To consider the reaction rates in the balance equations, a kinetic model was derived based on experimental reaction

kinetic data. Details of the experimental setup, the experimental results and the derived kinetic model can be found in the publication of Keller et al. (2011a).

All the equations of the process model were implemented in the commercial equation-oriented simulation environment Aspen Custom Modeler™, which uses an interface with Aspen Plus™ for the calculation of thermodynamic and physical properties. The UNIQUAC model was applied to consider nonideal liquid-phase behaviour (Abrams and Prausnitz, 1975). The vapour phase was described using the ideal gas law. The complete set of binary interaction parameters for the VLE calculations was previously presented by Keller et al. (2013) and is listed in Table A-2 of the Appendix.

#### 2.4. Process analysis

To gain detailed insight into the behaviour of the pilot-scale RD column, systematic simulation studies were performed using the validated process model described above. The effect of the following decisive operational parameters on the column performance were analysed: reflux ratio ( $RR$ ), mass-specific distillate-to-feed ratio ( $DF_{mass}$ ), molar feed ratio ( $\chi_{EtOH/DMC}$ ) and catalyst molar fraction ( $\chi_{F,cat}$ ) in the feed. The effect of these operational parameters on the product selectivities and reactant conversions were studied.

To perform the simulations at the same column load as was used for the experimental investigations on the pilot-scale column, a total feed mass flow of  $\dot{m}_F = 4.0$  kg/h was selected. During the process analysis, only one operational parameter was varied at once. The other parameters used the following default values:  $RR = 2.0$ ,  $DF_{mass} = 0.5$ ,  $\chi_{EtOH/DMC} = 4$ , and  $\chi_{F,cat} = 2 \cdot 10^{-3}$  mol/mol. The results of the process analysis are illustrated in Figure 2.

Figure 2a shows the results for the variation of the reflux ratio  $RR$  on the product selectivities and reactant conversions. At a higher reflux ratio, the selectivity towards DEC increases because EtOH is transported back to the column, particularly to the reactive section, thus increasing the amount of EtOH available for the second transesterification reaction. Despite a higher EtOH concentration in the reactive section, ethanol conversion shows only a negligible dependency on  $RR$  in the investigated operating range. DMC conversion even decreases significantly with an increasing  $RR$  because a change occurs in the catalyst concentration inside the reactive section. A higher  $RR$  under otherwise identical operational conditions causes higher internal liquid flow rates, resulting in a dilution of the homogeneous catalyst in the reactive section. The reaction rate is therefore lowered, relativising the positive effect of the higher EtOH concentration in the reactive section on the reactant conversions.

Figure 2b presents the results for the variation of the mass-specific distillate-to-feed ratio  $DF_{mass}$  on the product selectivities and reactant conversions. Higher distillate-to-feed ratios result in the stripping of EtOH out of the bottom of the column, thus increasing ethanol concentration in the reactive section. The selectivity towards DEC is therefore improved. However, no further improvement is observed for the values of  $DF_{mass} \geq 0.7$ . On the contrary, a slight decrease of DEC selectivity is even observed because significant amounts of DMC are stripped out of the reactive section at higher  $DF_{mass}$  values. Consequently, DMC is not available as a reactant in large parts of the reactive section, so no reaction occurs in the major portion of the reactive area. As a consequence, the selectivity towards the product of the first reaction, EMC, is improved, whereas the selectivity of DEC decreases accordingly. Despite higher EtOH concentrations in the reactive section, EtOH conversion shows only a negligible dependence on  $DF_{mass}$  in the operating range. DMC conversion even decreases significantly with an increasing  $DF_{mass}$ . The same conclusion was reached in the previous discussion of the influence of a higher reflux ratio. Because of higher internal flow rates caused by an increased  $DF_{mass}$ , the homogeneous catalyst is diluted, thus reducing the reaction rate. The positive effect of a higher EtOH concentration on the reactant conversions in the reactive section is hereby relativised.

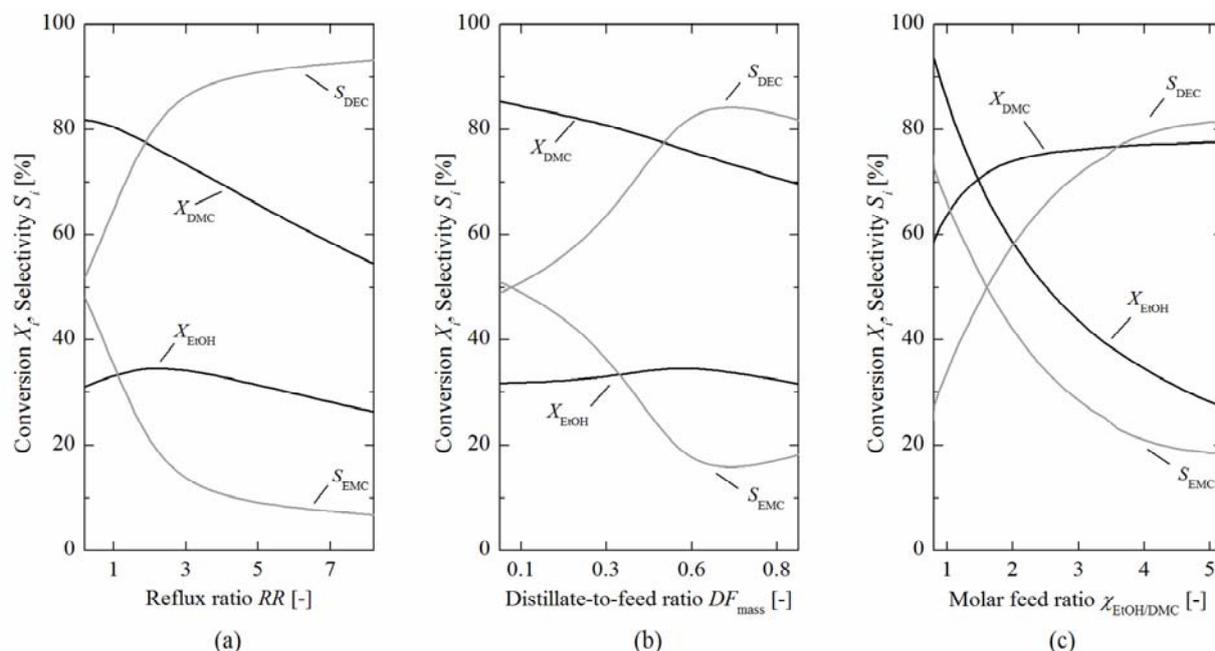


Fig. 2. Effect of decisive operational parameters on the reactant conversions and product selectivities. (a) Effect of the reflux ratio  $RR$ . (b) Effect of the mass-specific distillate-to-feed ratio  $DF_{mass}$ . (c) Effect of the molar feed ratio  $\chi_{EtOH/DMC}$ . Only a single operational parameter is varied. The other parameters have the following default values:  $RR = 2.0$ ,  $DF_{mass} = 0.5$ ,  $\chi_{EtOH/DMC} = 4.0$ ,  $\chi_{F,catal} = 2 \cdot 10^{-3}$  mol/mol

Figure 2c illustrates the strong impact of the molar feed ratio  $\chi_{EtOH/DMC}$  on the product selectivities and reactant conversions. Because the reflux ratio and the distillate-to-feed ratio are kept constant, EtOH accumulates in the entire column with an increased  $\chi_{EtOH/DMC}$ . Consequently, EtOH concentration in the reactive section increases, leading to an improvement in the DEC selectivity. Furthermore, higher EtOH concentrations in the reactive section cause an increase in DMC conversion. This is in contrast to the observations reported in the previous discussion of the effect of the reflux ratio and distillate-to-feed ratio. By varying the molar feed ratio, the internal flow rates do not change. Hence, the homogeneous catalyst is not diluted, and the positive effect of a higher EtOH concentration in the reactive section is not relativised. Consequently, increasing the molar feed ratio leads to an improved DMC conversion. As expected, lower EtOH conversion is obtained at a higher molar feed ratio.

### 3. OPTIMISATION

The process analysis demonstrated that reactant conversions and product selectivities can be affected significantly by the operational parameters of the RD column. In this section, optimisation studies are performed to determine the values of the operational parameters that lead to a maximised selectivity towards EMC or DEC while still having high reactant conversions. Before the results of the process optimisation are presented, a brief general overview of available optimisation strategies is given. Subsequently, the applied evolutionary algorithm is introduced, and the results of the optimisation studies are shown.

The optimisation of RD processes is usually a mixed-integer nonlinear programming (MINLP) problem, because of the nonlinear coupling of chemical reaction, transport phenomena and phase equilibria and the presence of discrete variables (Almeida-Rivera et al., 2004; Doherty and Malone, 2001). The latter are commonly used to decide the existence and/or type of a stage, e.g., feed stage, nonreactive or reactive stage (Gangadwala and Kienle, 2007). Different techniques to solve MINLP

problems have been developed and they can be classified into two main categories: deterministic and stochastic methods.

Deterministic algorithms derive reproducible new values from known values to find the optimum along a deterministic path. In contrast, stochastic algorithms employ probabilistic methods in their search, so that the solution path is stochastic and not reproducible. Several deterministic approaches are reported in the literature to optimise RD processes. For example, Gangadwala et al. (2007) applied the branch-and-bound approach (Dakin, 1965) to optimise the RD process for *n*-butyl acetate synthesis with respect to the total process costs. An outer-approximation algorithm (Duran and Grossmann, 1986) was successfully applied by Frey et al. (2000) and Poth et al. (2003) for the optimisation of the heterogeneously catalysed methyl acetate synthesis. Ciric et al. (1994) successfully used a generalised Bender decomposition algorithm (Geoffrion, 1972) to optimise an RD column for ethylene glycol synthesis.

The aforementioned deterministic optimisation algorithms are powerful algorithms but they can guarantee a global optimum as a solution only if the objective function is continuous and convex (Edgar et al., 2001). However, the convexity constraint is extremely limiting in the optimisation of RD processes (and of chemical engineering processes in general) due to the highly nonlinear character of the process. Because deterministic optimisation algorithms are gradient-based methods, they tend to converge into local optima unless the initial guesses for the start values were close to the global optimum. Therefore, stochastic optimisation algorithms have been developed that employ probabilistic methods in their search to escape from local optima. Moreover, stochastic optimisation methods are easy to implement and do not require the calculation of derivatives of the objective function, making the optimisation procedure very robust, which is especially advantageous for the optimisation of large-scale, nonlinear, nonconvex problems. The two most important examples of stochastic algorithms that were used to optimise RD processes are the simulated annealing method (Cardoso et al., 2000; Gomez et al., 2006; Kiss et al., 2012) and evolutionary algorithms (Babu and Khan, 2007; Rahman et al., 2008; Urselmann et al., 2011). An evolutionary algorithm was applied in the present work to optimise the RD column described in Section 2.2 towards EMC or DEC selectivity while still having high reactant conversions.

### 3.1. Applied evolutionary algorithm

Evolutionary algorithms are inspired by natural evolution. According to Darwin's theory of *survival of the fittest*, the individuals of a population that have best adapted to their environment have a higher chance to survive. These fittest individuals are naturally selected to produce offspring, and thereby pass on their genes to subsequent generations. Adaption to the environment takes place via the genetic operators of recombination and mutation that randomly change the genetic material of the offspring. If a genetic change proves to be successful, the genetic change will prevail over the long term through the creation of new and more adapted individuals. This natural interplay between the variation of individuals and the preference of the best individuals by selection is imitated by the evolutionary algorithms to solve engineering optimisation problems (Baeck, 1996; Eiben and Smith, 2007).

An evolutionary algorithm is a population-based optimiser that searches for the global optimum simultaneously at different points in the solution space. Each point in the solution space consists of a vector of decision variables and is called an *individual*. Decision variables themselves can be considered as *genes* of the individual. The number of individuals is called a *population*. The algorithm applies so-called *variation operators* that mimic the biological phenomena of recombination and mutation on an abstract level. Furthermore, a *selection operator* is applied to imitate the biological model. The role of variation operators is to create new individuals from old individuals through recombination and mutation. The role of selection operators is to distinguish among individuals based

on their fitness and to decide which individuals are allowed to generate offspring (*selection of parents*) and to pass into the next generation (*selection of survivors*). The fitness of an individual is calculated using the objective function of the optimisation problem and represents the individual's chance of survival, or, more accurately, the individual's quality of how well it can solve the optimisation problem.

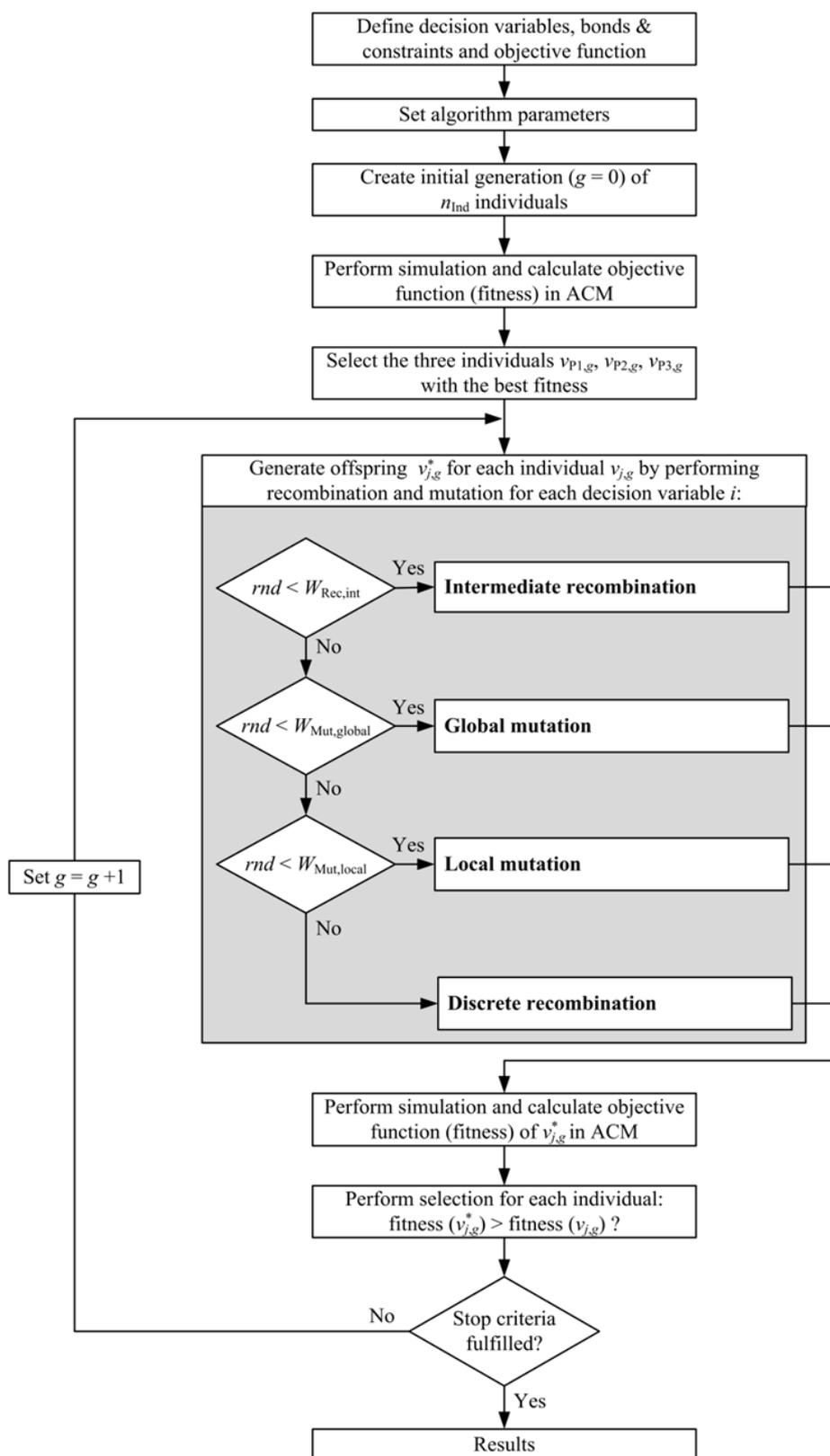


Fig. 3. Flowchart of the evolutionary algorithm applied in the present work to optimise the RD process

The algorithm used in the present work is implemented in the Visual Basic® for Applications (VBA) programming environment of Microsoft® Excel. The algorithm can be connected with the process simulator Aspen Custom Modeler® (ACM), in which the RD process model is implemented. Consequently, the optimisation itself is performed in VBA while the evaluation of the objective function is carried out in the process simulator ACM. The flowchart of the evolutionary algorithm is shown in Figure 3. Prior to starting the optimisation algorithm, the decision variables including their upper and lower bounds, the fitness function and the constraints of the optimisation problem must be defined. The following algorithm parameters must be defined: number of individuals per population ( $n_{Ind}$ ), maximum number of generations ( $n_{Gen}$ ), control parameters for recombination ( $W_{Rec\_int}$ ) and mutation ( $W_{Mut\_global}$ ,  $W_{Mut\_local}$ ) and the tolerance value ( $\Phi_{\Omega,max}$ ) used for the stop criteria. The algorithm starts with a random generation of an initial population featuring  $n_{Ind}$  individuals. In this context, the decision variables of the individuals are randomly initialised within their bounds using uniformly distributed random numbers. Random generation is important to ensure a high diversity of individuals in the initial population. The objective function (fitness) for all individuals of the initial generation is then calculated using the RD model implemented in ACM. After this initialisation routine, the population is modified from generation to generation by replacing one or more individuals with new solutions (called offspring). The main task of an evolutionary algorithm is to generate one offspring  $v_{j,g}^*$  for each individual  $v_{j,g}$ . The offspring then compete with each other for a free place in the next generation. The offspring  $v_{j,g}^*$  are generated by executing the following variation operators for each decision variable  $i$ :

- intermediate recombination,
- global mutation (in the complete solution space),
- local mutation (in the vicinity of the decision variables),
- discrete recombination.

The three individuals with the best fitness are chosen because their decision variables are used to generate the offspring through recombination. These individuals are referred to as parents ( $v_{P1,g}$ ,  $v_{P2,g}$ ,  $v_{P3,g}$ ). A generated random number  $rnd$  is compared with the user-defined control parameter  $W_{Rec\_int}$  to decide whether the intermediate recombination takes place. In the case of intermediate recombination, the decision variable of the offspring is calculated by averaging the corresponding decision variable of each parent and that of the respective individual:

$$v_{i,j,g}^* = \frac{1}{4} (v_{i,P1,g} + v_{i,P2,g} + v_{i,P3,g} + v_{i,j,g}) \quad \text{if } rnd[0,1] < W_{Rec\_int}; i = 1, \dots, n_{Var}; j = 1, \dots, n_{Ind} \quad (1)$$

where  $v_{j,g}$  is the value of the decision variables  $i$  of individual  $j$  in generation  $g$  and  $v_{j,g}^*$  represents the analogue for the offspring.

If intermediate recombination does not occur, a new random number  $rnd$  is generated and compared with the control parameter  $W_{Mut\_global}$  for global mutation. In the case of global mutation, the decision variables of the offspring are generated randomly within its lower and upper bound ( $lb_i$ ,  $ub_i$ ):

$$v_{i,j,g}^* = lb_i + rnd[0,1] \cdot (ub_i - lb_i) \quad \text{if } rnd[0,1] < W_{Mut\_global}; i = 1, \dots, n_{Var}; j = 1, \dots, n_{Ind} \quad (2)$$

The third possibility to change the value of a decision variable is the execution of local mutation. In contrast to global mutation, which explores unseen regions of the complete solution space, local mutation discovers only the vicinity of the decision variable:

$$v_{i,j,g}^* = v_{i,j,g} \cdot (1 + \xi \cdot (2 \cdot rnd[0,1] - 1)) \quad \text{if } rnd[0,1] < W_{Mut\_local}; i = 1, \dots, n_{Var}; j = 1, \dots, n_{Ind} \quad (3)$$

The region within which local mutation can occur is delimited by the variable  $\xi$  which must be defined by the user and thus allows the mutation region to be set flexibly. To calculate the value of a decision

variable of the offspring, both mutation operators use a random number  $rnd$  which is each time newly generated and is therefore different to the random number that is generated to decide whether the corresponding mutation operator takes place.

The last variation operator, namely discrete recombination, occurs only with the probability:  $W_{Rek\_dis} = (1 - W_{Rek\_int}) \cdot (1 - W_{Mut\_global}) \cdot (1 - W_{Mut\_local})$ . Discrete recombination randomly selects the decision variable from the three fittest parents and the respective individual and transfers this value to the offspring.

$$v_{i,j,g}^* = rnd[v_{i,P1,g} + v_{i,P2,g} + v_{i,P3,g} + v_{i,j,g}]; \quad i = 1, \dots, n_{Var}; \quad j = 1, \dots, n_{Ind} \quad (4)$$

After the offspring are generated, their fitness is calculated in ACM. Subsequently, the selection takes place by comparing the fitness of each offspring with that of the respective parent. If the offspring is superior then it replaces its parent in the next generation  $g + 1$ . If the parent is superior, the parent advances unchanged to the next generation. The algorithm continues until the number of generations exceeds the maximal generation number  $n_{Gen}$  or the average fitness  $\bar{\Omega}_g^{av}$  of the generations has not changed for five generations:

$$\Phi_{\Omega,max} \geq \left| \sqrt{5 \cdot \bar{\Omega}_g^{av} - \sum_{k=g-5}^{g-1} \bar{\Omega}_k^{av}} \right| \quad (5)$$

Where  $\Phi_{\Omega,max}$  is a user-defined tolerance value.

The efficiency of an evolutionary algorithm depends strongly on the values of the control parameters. Different values of these control parameters might be optimal at different stages of the evolutionary process (Schwefel, 1981; Smith, 2008). For example, high mutation steps in the early stage of an evolutionary algorithm can help to explore the solution space extensively, whereas small mutation steps in the late stage can help to fine-tune the solution extensively. Various strategies have therefore been developed in the literature to alter the values of these control parameters during the course of evolution. According to Eiben et al. (2007), there are adaptive, self-adaptive and deterministic parameter-control techniques.

Table 3. Algorithm parameters applied for the optimisation of the pilot-scale RD column with respect to product selectivity. The control parameters were changed after a certain number of generations  $g$

Number of individuals per population, $n_{Ind}$	13			
Number of maximal generations, $n_{Gen}$	300			
Tolerance value, $\Phi_{\Omega,max}$	$1 \cdot 10^{-7}$			
Control parameters	Phase 1	Phase 2 ( $g = 75$ )	Phase 3 ( $g = 90$ )	Phase 4 ( $g = 105$ )
Intermediate recombination, $W_{Rec\_int}$	0.2	0.5	0.0	0.5
Global mutation, $W_{Mut\_global}$	0.9	0.3	0.0	0.3
Local mutation, $W_{Mut\_local}$	0.4	0.3	0.9	0.1
Radius for local mutation, $\xi$	1	0.1	0.01	0.005

Adaptive parameter control uses some feedback from the search to determine the direction or magnitude of the change to the control parameters. In the case of self-adaptive parameter control, the control parameters themselves undergo mutation and recombination during the search. Deterministic

methods alter the values of the control parameters by a fixed schedule without using any feedback from the search progress. In this work, the concept of deterministic parameter control was used by changing the values of the control parameters after a certain number of generations. The values, which are listed in Table 3, were reasonably chosen such that the following strategy is ensured: in the first phase of the optimisation run, the probability of global mutation is relatively high to explore the solution space extensively, whereas the second phase is dominated by recombination to inherit the properties of the fittest parents to their offspring. Local mutation is applied intensively in the third phase to discover the vicinity of each individual. The last phase is again dominated by recombination.

### 3.2. Objective and penalty functions

The evolutionary algorithm presented above is used in this article to optimise the operational parameters of the pilot-scale RD column for the homogeneously catalysed transesterification of DMC with EtOH. The optimisation studies are conducted to maximise the product selectivity. As the reaction system consists of two target products, two optimisation studies are performed, namely those towards EMC and towards DEC selectivity.

The objective function for the optimisation towards EMC selectivity ( $S_{EMC}$ ) is

$$Z = \min(\Omega_{s,EMC}) = \min(-S_{EMC} + Pen_{VL} + Pen_{LL} + Pen_{cat} + Pen_{conversion} + Pen_{purity,EMC}) \quad (6)$$

whereas the objective function for the optimisation towards DEC selectivity ( $S_{DEC}$ ) is:

$$Z = \min(\Omega_{s,DEC}) = \min(-S_{DEC} + Pen_{VL} + Pen_{LL} + Pen_{cat} + Pen_{conversion} + Pen_{purity,DEC}) \quad (7)$$

The duality principle (Deb, 2005) was applied to convert the maximisation problem into a minimisation problem by multiplying the objective function by -1.

As evolutionary algorithms cannot account directly for constraints, so-called *penalty functions* are formulated for each constraint. If a solution does not fulfil a constraint, a penalty value  $Pen_j$  for that constraint violation is added to the objective function value (Schwefel, 1995). The penalty functions used in the present work are presented below.

Optimisation is performed under the constraints that the vapour load ( $VL$ ) and liquid load ( $LL$ ) of the RD column are always within the proper range of the applied structured Sulzer BXTM packing. Quadratic penalty functions are used to account for the case that the vapour and liquid loads of the column are outside the proper range:

$$Pen_{VL} = \begin{cases} 10 + 10 \cdot (1 - VL / VL_{min})^2, & \text{if } VL < VL_{min} \\ 10 + 10 \cdot (VL - VL_{max})^2, & \text{if } VL > VL_{max} \\ 0, & \text{otherwise.} \end{cases} \quad (8)$$

$$Pen_{LL} = \begin{cases} 10 + 10 \cdot (1 - LL / LL_{min})^2, & \text{if } LL < LL_{min} \\ 0, & \text{otherwise.} \end{cases} \quad (9)$$

These penalty functions aim at preventing unfavourable operating conditions from being selected as optimal solutions. In the case of the structured Sulzer BXTM packing, the lower and upper limit values for the vapour loads are  $VL_{min} = 0.2 \cdot Pa^{0.5}$  and  $VL_{max} = 2.5 \cdot Pa^{0.5}$  (Kister, 1992). Because the liquid load is usually not the limiting factor in the case of structured packings, only the lower value of  $LL_{min} = 0.05 \text{ m}^3/(\text{m}^3 \text{ h})$  is taken into account (Sulzer Chemtech, 2004).

In one of our previous articles, we found that a small amount of water brought in by the chemicals reacts with the catalyst sodium ethoxide to form sodium carbonate (Keller et al., 2011a). The molar fraction  $x_{cat}$  of the homogeneous catalyst sodium ethoxide inside the column should always be higher than  $x_{cat,min} = 4 \cdot 10^{-4}$  mol/mol to compensate for its consumption. The penalty function enforcing the catalyst molar fraction constraint is calculated by the following:

$$Pen_{cat} = \begin{cases} 25 + 100 \cdot \left( \frac{1 - x_{cat}}{x_{cat,min}} \right)^2 & , \text{if } x_{cat} > x_{cat,min} \\ 0 & , \text{otherwise} \end{cases} \quad (10)$$

Note that the pre-factors of the penalty functions in Eqs. 8–10 are selected with respect to the expected order of magnitude of the selectivity that is obtained.

The optimisation aims to find the operation point of the column where the highest selectivity of the target product is achieved. However, the operating point should also guarantee high reactant conversions and product purities, so the following penalty functions for reactant conversion and product purity are used:

$$Pen_{conversion} = 30 \cdot \exp(-0.06 \cdot X_{EtOH}) + 30 \cdot \exp(-0.06 \cdot X_{DMC}) \quad (11)$$

$$Pen_{purity,i} = 20 \cdot \exp(-0.06 \cdot w_{B,i}) \quad (12)$$

Where  $w_{B,i}$  is the mass fraction of the target product, EMC or DEC, in the bottom stream. These exponential penalty functions ensure that relatively high penalty values are calculated at low conversions or purities. In contrast, if high conversions or purities are obtained, the calculated penalty values are low.

The optimisation studies are restricted solely to operational parameters and not to structural parameters of the pilot-scale RD column. A description of the column setup is found in Section 2.2. The decision variables that are considered in the optimisation studies are listed together with their bounds in Table 4. The total feed flow to the column was fixed to 4.0 kg/h. The values of the algorithm parameters applied for the optimisation studies are listed in Table 3.

Table 4. Decision variables considered in the optimisation of the pilot-scale RD column with respect to product selectivity. The bounds of each decision variable are also given

Decision variable	Lower and upper bound
Reflux ratio, $RR$ [-]	$0.20 < RR < 7.00$
Distillate-to-feed ratio, $DF_{mass}$ [-]	$0.050 < DF_{mass} < 0.700$
Molar feed ratio, $\chi_{EtOH/DMC}$ [-]	$0.20 < \chi_{EtOH/DMC} < 6.00$
Catalyst molar fraction <sup>a</sup> , $x_{F,cat}$ [mol/mol]	$0.001 < x_{F,cat} < 0.020$

<sup>a</sup> Molar fraction with respect to the total feed stream

### 3.3. Optimisation towards DEC selectivity

First, the optimisation results with respect to DEC selectivity are discussed. The results shown in Table 5 demonstrate that RD allows the production of DEC with a high selectivity of  $S_{DEC}^{RD} = 95$  %. Because DEC is the product of the second transesterification reaction, the operational parameters must be selected so that the concentration of EtOH in the reactive section is high. Hence, a high reflux ratio, a comparatively high distillate-to-feed ratio and catalyst molar fraction are required. For the selective

production of DEC in the pilot-scale column, a relatively low molar feed ratio of  $\chi_{EtOH/DMC}^{RD} = 2.18$  is required. Both reactant conversions with values of  $X_{EtOH}^{RD} = 77\%$  and  $X_{DMC}^{RD} = 86\%$  are sufficiently high. For comparison: a batch reactor would reach, even at a high stoichiometric ratio of  $\chi_{EtOH/DMC}^{Batch} = 10$ , only a selectivity of  $S_{DEC}^{Batch} = 66\%$ . The conversion of DMC would be at  $X_{DMC}^{Batch} = 97\%$ , but EtOH conversion would be at just  $X_{EtOH}^{Batch} = 16\%$ . These results show that the RD column is an attractive alternative to produce DEC at a high selectivity while still having high reactant conversions. The purity of DEC in the bottom stream of the column is relatively high with a value of  $w_{B,DEC}^{RD} = 92\%$ .

Table 5. Optimisation results of the pilot-scale RD column to produce EMC or DEC

Results	Optimisation	
	EMC	DEC
Selectivity of EMC, $S_{EMC}$ [%]	95	5
Selectivity of DEC, $S_{DEC}$ [%]	5	95
Conversion of EtOH, $X_{EtOH}$ [%]	97	77
Conversion of DMC, $X_{DMC}$ [%]	30	86
Reflux ratio, $RR$ [-]	4.75	5.12
Distillate-to-feed ratio, $DF_{mass}$ [-]	0.14	0.45
Molar feed ratio, $\chi_{EtOH/DMC}$ [-]	0.32	2.18
Catalyst molar fraction <sup>a</sup> , $x_{F,cat}$ [mol/mol]	0.007	0.020

<sup>a</sup> Molar fraction with respect to the total feed stream

### 3.4. Optimisation towards EMC selectivity

The optimisation results in Table 5 show that also EMC can be produced in the pilot-scale RD column with a selectivity of  $S_{EMC}^{RD} = 95\%$ . EMC is the product of the first transesterification reaction. Consequently, a low molar feed ratio of  $\chi_{EtOH/DMC}^{RD} = 0.32$  is needed. A high reflux ratio is required to transport DMC back to the reactive section. The distillate-to-feed ratio is comparatively low because otherwise EtOH is stripped out of the reactive section. A low catalyst molar fraction is required to favour the selectivity towards EMC. Because of the high excess of DMC in the feed stream, an almost complete conversion of EtOH with a value of  $X_{EtOH}^{RD} = 97\%$  is achieved in the pilot-scale column. In contrast, the conversion of DMC with a value of  $X_{DMC}^{RD} = 30\%$  is relatively low. For comparison: a batch reactor would need a stoichiometric ratio of  $\chi_{EtOH/DMC}^{RD} = 0.2$  to reach the same selectivity towards EMC. In this case, the conversion of EtOH would be at  $X_{EtOH}^{Batch} = 91\%$  whereas the conversion of DMC would be at just  $X_{DMC}^{Batch} = 17\%$ . These results show that the RD column is an attractive alternative to produce EMC at a high selectivity while still having high EtOH conversions. The DMC conversion is, however, relatively low.

To further increase DMC conversion, a higher molar feed ratio would be necessary. In this case, however, the selectivity towards EMC would be decreased. The maximisation of EMC selectivity and DMC conversion are conflicting objectives because higher DMC conversions are possible only if lower EMC selectivities are accepted. Therefore, a multi-objective optimisation study was performed, to

determine the optimal combinations of EMC selectivity and DMC conversion that can be obtained in the pilot-scale RD column. In the case of multi-objective optimisation problems, a single optimal solution is not obtained but multiple optimal solutions, each representing a trade-off between the conflicting objectives (Deb, 2004). The weighted-sum method (Zadeh, 1963) was applied for the multi-objective optimisation study to determine the optimal combinations of EMC selectivity and DMC conversion. This method transforms the multi-objective optimisation problem into a single-objective optimisation problem by pre-multiplying each objective with a user-supplied weighting factor  $\omega_i$ :

$$\begin{aligned} Z &= \min(\omega_{EMC} \cdot \Omega_{S,EMC} + \omega_{DMC} \cdot \Omega_{X,DMC}) \\ &= \min(-\omega_{EMC} \cdot S_{EMC} - \omega_{DMC} \cdot X_{DMC} + Pen_{VL} + Pen_{LL} + Pen_{cat} + Pen_{purity,EMC}) \end{aligned} \quad (13)$$

Overall, 11 optimisation runs were performed by varying the weighting factor  $\omega_{EMC}$  in 0.1 steps from 0 to 1. The second weighting factor was accordingly:  $\omega_{DMC} = 1 - \omega_{EMC}$ .

Each optimisation run gives a so-called Pareto-optimal solution and all of the Pareto-optimal solutions form the Pareto front, which is presented in Figure 4. As can be seen, in the presence of multiple Pareto-optimal solutions, one solution is difficult to choose over another without any further information about the problem because one solution is better than the other for one objective but is worse for the other objectives. However, using the Pareto-front, an optimal operating point can be selected depending on whether high EMC selectivities or high DMC conversions are preferred.

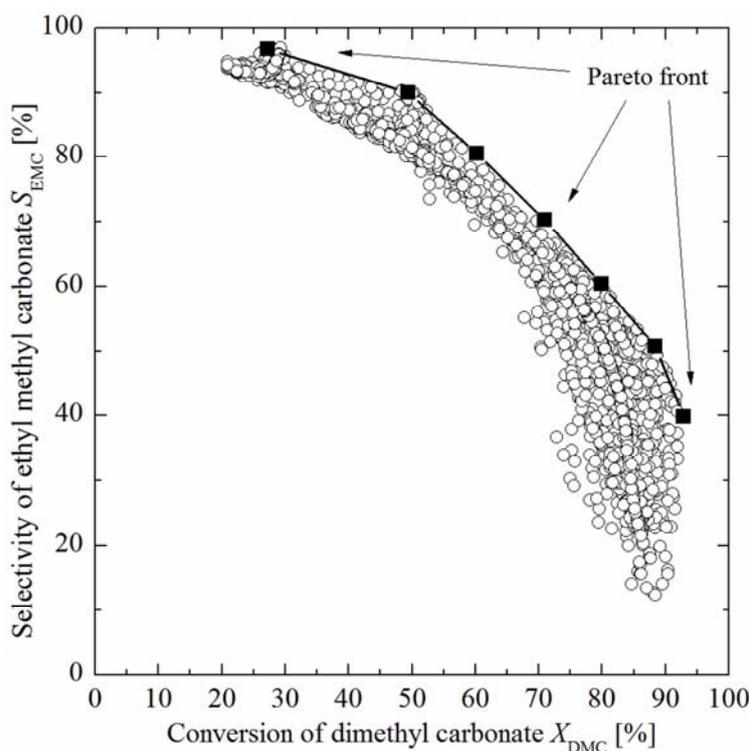


Fig. 4. Pareto front obtained from the multi-objective optimisation of the pilot-scale RD column with respect to EMC selectivity and DMC conversion. In addition to the Pareto-optimal solutions (■), further solutions (○) that were studied by the evolutionary algorithm during the optimisation process are given.

#### 4. CONCLUSIONS

In the present article, a validated reactive distillation process model was used for a detailed process analysis of the transesterification of dimethyl carbonate with ethanol in a pilot-scale reactive distillation column. In this context, the effect of the following operational parameters on the column behaviour was studied: reflux ratio, mass-specific distillate-to-feed ratio, molar feed ratio and catalyst molar fraction

in the feed. The process analysis demonstrated that reactant conversions and product selectivities can be significantly affected by the operational parameters of the column.

The operational parameters of the pilot-scale reactive distillation column were optimised to maximise the selectivity towards ethyl methyl carbonate and diethyl carbonate. An evolutionary algorithm was successfully applied for these optimisation studies. The results showed that diethyl carbonate can be produced in the pilot-scale reactive distillation column with a selectivity of  $S_{DEC}^{RD} = 95\%$  while still having high reactant conversions of  $X_{EtOH}^{RD} = 77\%$  and  $X_{DMC}^{RD} = 86\%$ . Ethyl methyl carbonate can also be produced in the pilot-scale reactive distillation column with a selectivity of  $S_{EMC}^{RD} = 95\%$ . An almost complete conversion of ethanol ( $X_{EtOH}^{RD} = 97\%$ ) is achieved but the conversion of dimethyl carbonate with a value of  $X_{DMC}^{RD} = 30\%$  is relatively low.

A multi-objective optimisation study was therefore performed to determine the Pareto-optimal combinations of ethyl methyl carbonate selectivity and dimethyl carbonate conversion that can be obtained in the pilot-scale reactive distillation column. The Pareto-front was successfully calculated applying the weighted-sum method.

## SYMBOLS

$a_i$	activity of component $i$ , mol/mol
$DF_{mass}$	mass-specific distillate-to-feed ratio, -
$lb_i$	lower bound of decision variable $i$ , -
$c$	concentration, $\text{kg m}^{-3}$
$n_{Gen}$	number of generations, -
$n_{Ind}$	number of individuals per population, -
$n_{Var}$	number of decision variables, -
$Pen$	penalty function, -
$P$	pressure, kPa
$rnd$	random number, -
$RR$	reflux ratio, -
$S_{DEC}$	selectivity towards diethyl carbonate, %
$S_{EMC}$	selectivity towards ethyl methyl carbonate, %
$T_b$	boiling temperature, K
$ub_i$	upper bound of decision variable $i$ , -
$v$	decision variable vector (called individual), -
$v^*$	newly generated decision variable vector (called offspring), -
$W_{Mut\_global}$	control parameter for global mutation, -
$W_{Mut\_local}$	control parameter for local mutation, -
$W_{Rec\_dis}$	control parameter for discrete recombination, -
$W_{Rec\_int}$	control parameter for intermediate recombination, -
$w$	mass fraction in the liquid phase, kg/kg
$x$	molar fraction in the liquid phase, mol/mol
$X_{DMC}$	conversion of dimethyl carbonate, %
$X_{EtOH}$	conversion of ethanol, %
$Z$	optimisation problem, -

### Greek symbols

$\gamma_i$	activity coefficient of component $i$ in the liquid phase, -
$\chi_{EtOH/DMC}$	molar feed ratio between EtOH and DMC, -

$\xi$	radius of local mutation, -
$\Phi_{\Omega, max}$	tolerance value used for the stop criteria of the evolutionary algorithm, -
$\Omega$	objective function, -
$\omega$	weighting factor, -

### Subscripts

$B$	bottom stream
$cat$	catalyst
$F$	feed
$g$	generation $g$
$i$	decision variable $i$
$j$	individual $j$
$LL$	liquid load
$S$	selectivity
$VL$	vapour load
$X$	conversion

### Abbreviations

ACM	Aspen Custom Modeler <sup>®</sup>
CAS	Chemical Abstracts Service
DEC	diethyl carbonate
DMC	dimethyl carbonate
EMC	ethyl methyl carbonate
EQ	equilibrium-stage model
EtOH	ethanol
MeOH	methanol
MINLP	mixed-integer nonlinear programming
MTBE	methyl <i>tert</i> -butyl ether
NEQ	nonequilibrium-stage model
R1	transesterification of dimethyl carbonate with ethanol to ethyl methyl carbonate and methanol
R2	transesterification of ethyl methyl carbonate with ethanol to diethyl carbonate and methanol
RD	reactive distillation
UNIQUAC	universal quasichemical
VBA	Visual Basic <sup>®</sup> for Applications

### REFERENCES

- Abrams D.S., Prausnitz J.M., 1975. Statistical thermodynamics of liquid mixtures: A new expression for the excess energy of partly or completely miscible systems. *AIChE J.*, 21, 116–128. DOI: 10.1002/aic.690210115.
- Agreda V.H., Partin L.R., Heise W.H., 1990. High-purity methyl acetate via reactive distillation. *Chem. Eng. Prog.*, 86, 40–46.
- Almeida-Rivera C.P., Swinkels P.L.J., Grievink J., 2004. Designing reactive distillation processes: Present and future. *Comput. Chem. Eng.*, 28, 1997–2020. DOI: 10.1016/j.compchemeng.2004.03.014.
- Babu B.V., Khan M., 2007. Optimisation of reactive distillation processes using differential evolution strategies. *Asia-Pac. J. Chem. Eng.*, 2, 322–335. DOI: 10.1002/apj.89.
- Baeck T., 1996. *Evolutionary algorithms in theory and practice. Evolution strategies, evolutionary programming, genetic algorithms*. 1<sup>st</sup> edition, Oxford Univ. Press, New York.

- Bolon D.A., Hallgren J.E., 1984. Synthesis of polycarbonate from dialkyl carbonate and bisphenol diester. U.S. Patent No. 4452968. General Electric Co., USA.
- Bravo J.L., Rocha J.A., Fair, J.R., 1985. Mass transfer in gauze packings. *Hydrocarbon Process.* 64, 91–95.
- Burghardt A., Warmuziński K., Buzek J., Pytlik A., 1983. Diffusional models of multicomponent distillation and their experimental verification. *Chem. Eng. J.*, 26, 71–84. DOI: 10.1016/0300-9467(83)80001-X.
- Cardoso M.F., Salcedo R.L., Feyo de Azevedo S., Barbosa D., 2000. Optimisation of reactive distillation processes with simulated annealing. *Chem. Eng. Sci.*, 55, 5059–5078. DOI: 10.1016/S0009-2509(00)00119-6.
- Chilton T.H., Colburn A.P., 1935. Distillation and absorption in packed columns: A convenient design and correlation method. *J. Ind. Eng. Chem.*, 27, 255–260. DOI: 10.1021/ie50303a004.
- Ciric A.R., Gu D., 1994. Synthesis of nonequilibrium reactive distillation processes by MINLP optimisation. *AIChE J.*, 40, 1479–1487. DOI: 10.1002/aic.690400907.
- Dakin R.J., 1965. A tree-search algorithm for mixed integer programming problems. *Computer Journal*, 8, 250–255. DOI: 10.1093/comjnl/8.3.250.
- Deb K., 2004. *Multi-objective optimisation using evolutionary algorithms*. 1st edition, Wiley-VCH, Chichester.
- Deb K., 2005. *Optimisation for engineering design*. 8th edition, Prentice-Hall, New Delhi.
- Ding M.S., Xu K., Zhang S.S., Amine K., Henriksen G.L., Jow T.R., 2001. Change of conductivity with salt content, solvent composition, and temperature for electrolytes of 1 LiPF<sub>6</sub> in ethylene carbonate-ethyl methyl carbonate. *J. Electrochem. Soc.*, 148, A1196. DOI: 10.1149/1.1403730.
- Doherty M.F., Malone M.F., 2001. *Conceptual design of distillation systems*. 1st edition, McGraw-Hill, Boston, Mass.
- Dunn B.C., Guenneau C., Hilton S.A., Pahnke J., Eyring E.M., Dworzanski J., Meuzelaar H.L.C., Hu J.Z., Solum M.S., Pugmire R.J., 2002. Production of diethyl carbonate from ethanol and carbon monoxide over a heterogeneous catalyst. *Energy Fuels*, 16, 177–181. DOI: 10.1021/ef0101816.
- Duran M.A., Grossmann I.E., 1986. An outer-approximation algorithm for a class of mixed-integer nonlinear programs. *Math. Program*, 36, 307–339. DOI: 10.1007/BF02592064.
- Edgar T.F., Himmelblau D.M., Lasdon L.S., 2001. *Optimisation of chemical processes*. 2nd edition, McGraw-Hill, Boston.
- Eiben A.E., Smith J.E., 2007. *Introduction to evolutionary computing*. 2nd edition, Springer, Berlin.
- Frey T., Stichlmair J., 2000. MINLP-Optimierung von Reaktivrektifikationskolonnen. *Chem. Ing. Tech.*, 72, 1102. DOI: 10.1002/1522-2640(200009)72:9<1102::AID-CITE11020>3.0.CO;2-A.
- Gangadwala J., Kienle A., 2007. MINLP optimisation of butyl acetate synthesis. *Chem. Eng. Process.*, 46, 107–118. DOI: 10.1016/j.cep.2006.04.009.
- Geoffrion A.M., 1972. Generalized Benders decomposition. *J. Optim. Theory Appl.*, 10, 237–260. DOI: 10.1007/BF00934810.
- Gmehling J., Onken U., 2002. *Carboxylic acids, anhydrides*. Supplement 1. 1st edition, DECHEMA, Frankfurt am Main.
- Gmehling J., Onken U., Arlt W., 1977. *Organic hydroxy compounds: alcohols*. 1st edition, DECHEMA, Frankfurt am Main.
- Gomez J.M., Reneaume J.M., Meyer M., Meyer X., 2006. MINLP optimisation of catalytic distillation columns using a rate-based model, In: Sørensen E. (Ed.), *Proc. of the Conf. Distillation and Absorption 2006*. Institution of Chemical Engineers, Rugby, 820–829.
- González-Ruggerio C.A., Keller T., Pilarczyk J., Sałacki W., Górak A., 2012. TAEE synthesis from isoamylenes and ethanol by catalytic distillation: Pilot plant experiments and model validation. *Fuel Process Technol.* 102, 1–10. DOI: 10.1016/j.fuproc.2012.04.012.
- Górak A., Hoffmann A., 2001. Catalytic distillation in structured packings: methyl acetate synthesis. *AIChE J.*, 47, 1067–1076. DOI: 10.1002/aic.690470513.
- Górak A., Stankiewicz A., 2011. Intensified reaction and separation systems. *Annu. Rev. Chem. Biomol. Eng.*, 2, 431–451. DOI: 10.1146/annurev-chembioeng-061010-114159.
- Hasabnis A., Mahajani S., 2010. Entrainer-based reactive distillation for esterification of glycerol with acetic acid. *Ind. Eng. Chem. Res.*, 49, 9058–9067. DOI: 10.1021/ie100937p.
- Hoffmann A., Noeres C., Górak A., 2004. Scale-up of reactive distillation columns with catalytic packings. *Chem. Eng. Process.*, 43, 383–395. DOI: 10.1016/S0255-2701(03)00121-1.
- Keller T., Górak A., 2013. Modelling of homogeneously catalysed reactive distillation processes in packed columns: Experimental model validation. *Comp. Chem. Eng.*, 48. DOI: 10.1016/j.compchemeng.2012.07.015.

- Keller T., Holtbruegge J., Górak A., 2012. Transesterification of dimethyl carbonate with ethanol in a pilot-scale reactive distillation column. *Chem. Eng. J.*, 180, 309–322. DOI: 10.1016/j.cej.2011.11.072.
- Keller T., Holtbruegge J., Niesbach A., Górak A., 2011a. Transesterification of dimethyl carbonate with ethanol to form ethyl methyl carbonate and diethyl carbonate: A comprehensive study on chemical equilibrium and reaction kinetics. *Ind. Eng. Chem. Res.*, 50, 11073–11086. DOI: 10.1021/ie2014982.
- Keller T., Muendges J., Jantharasuk A., González-Ruggerio C., Moritz H., Kreis P., Górak A., 2011b. Experimental model validation for *n*-propyl propionate synthesis in a reactive distillation column coupled with a liquid–liquid phase separator. *Chem. Eng. Sci.*, 66, 4889–4900. DOI: 10.1016/j.ces.2011.06.056.
- Kenig E.Y., Bäder H., Górak A., Bessling B., Adrian T., Schoenmakers H., 2001. Investigation of ethyl acetate reactive distillation process. *Chem. Eng. Sci.*, 56, 6185–6193. DOI: 10.1016/S0009-2509(01)00206-8.
- Kenig E.Y., Górak A., 2007. Modeling of reactive distillation. In: Keil F. (Ed.), *Modeling of process intensification*, 1st edition, Wiley-VCH, Weinheim, 323–364.
- Kiss A.A., Segovia-Hernández J.G., Bildea C.S., Miranda-Galindo E.Y., Hernández S., 2012. Reactive DWC leading the way to FAME and fortune. *Fuel*, 95, 352–359. DOI: 10.1016/j.fuel.2011.12.064.
- Kister H.Z., 1992. *Distillation design*. 1st edition, McGraw-Hill, New York.
- Kloeker M., Kenig E.Y., Hoffmann A., Kreis P., Górak A., 2005. Rate-based modelling and simulation of reactive separations in gas/vapour-liquid systems. *Chem. Eng. Process.* 44, 617–629. DOI: 10.1016/j.cep.2003.12.011.
- Leino E., Mäki-Arvela P., Eta V., Murzin D.Y., Salmi T., Mikkola J.-P., 2010. Conventional synthesis methods of short-chain dialkylcarbonates and novel production technology via direct route from alcohol and waste CO<sub>2</sub>. *Appl. Catal.*, A 383, 1–13. DOI: 10.1016/j.apcata.2010.05.046.
- Lewis W.K., Whitman W.G., 1924. Principles of gas absorption. *Ind. Eng. Chem. Res.*, 16, 1215–1220. DOI: 10.1021/ie50180a002.
- Luo H.-P., Xiao W.-D., 2001. A reactive distillation process for a cascade and azeotropic reaction system: Carbonylation of ethanol with dimethyl carbonate. *Chem. Eng. Sci.*, 56, 403–410. DOI: 10.1016/S0009-2509(00)00242-6.
- Luo H.-P., Xia, W.-D., Zhu K.-H., 2000. Isobaric vapour-liquid equilibria of alkyl carbonates with alcohols. *Fluid Phase Equilib.*, 175, 91–105. DOI: 10.1016/S0378-3812(00)00444-1.
- Marshall S., Ratnakumar B., Subbarao S., 2011. Ethyl methyl carbonate as a cosolvent for lithium-ion cells. *NASA Tech Briefs*. Retrieved May 2011 from <http://www.nasatech.com/Briefs/June01/NPO20605.html>.
- Mueller I., Kenig E.Y., 2007. Reactive distillation in a dividing wall column: rate-based modeling and simulations. *Ind. Eng. Chem. Res.*, 46, 3709–3719. DOI: 10.1021/ie0610344.
- NIST, 2009. *Chemistry web book*. Retrieved December 2009 from <http://webbook.nist.gov/chemistry>.
- Noeres C., Kenig E.Y., Górak A., 2003. Modelling of reactive separation processes: reactive absorption and reactive distillation. *Chem. Eng. Process.*, 42, 157–178. DOI: 10.1016/S0255-2701(02)00086-7.
- Okuno H., Koshina H., Morita A., 1996. Secondary nonaqueous-electrolyte battery. U.S. Patent No. 5521027. Matsushita Electric Industrial Co., Ltd., Japan.
- Orjuela A., Kolah A., Hong X., Lira C.T., Miller D.J., 2011. Diethyl succinate synthesis by reactive distillation. *Sep. Purif. Technol.*, 88, 151–162. DOI: 10.1016/j.seppur.2011.11.033.
- Pacheco M.A., Marshall C.L., 1997. Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive. *Energy Fuels*, 11, 2–29. DOI: 10.1021/ef9600974.
- Plichta E.J., Behl W.K., 2000. A low-temperature electrolyte for lithium and lithium-ion batteries. *J. Power Sources*, 88, 192–196. DOI: 10.1016/S0378-7753(00)00367-0.
- Poth N., Brusis D., Stichlmair J., 2003. Rigorous optimisation of reactive distillation in GAMS with the use of external functions. *Comput. Aided Chem. Eng.*, 14, 869–874. DOI: 10.1016/S1570-7946(03)80226-2.
- Rahman I., Ahmad A., Kuma P., Kulkarni B.D., 2008. Optimisation of a continuous process for the recovery of lactic acid using differential evolution algorithm. *Chem. Prod. Process Model.*, 3, 6. DOI: 10.2202/1934-2659.1111.
- Rocha J.A., Bravo J.L., Fair J.R., 1993. Distillation columns containing structured packings: a comprehensive model for their performance: hydraulic models. *Ind. Eng. Chem. Res.*, 32, 641–651. DOI: 10.1021/ie00016a010.
- Rodríguez A., Canosa J., Domínguez A., Tojo J., 2002. Vapour-liquid equilibria of dimethyl carbonate with linear alcohols and estimation of interaction parameters for the UNIFAC and ASOG method. *Fluid Phase Equilib.*, 201, 187–201. DOI: 10.1016/S0378-3812(02)00201-7.

- Rodríguez A., Canosa J., Domínguez A., Tojo J., 2003. Isobaric phase equilibria of diethyl carbonate with five alcohols at 101.3 kPa. *J. Chem. Eng. Data*, 48, 86–91. DOI: 10.1021/je0201018.
- Schmidt-Traub H., Górak A., 2006. *Integrated reaction and separation operations*. 1st edition, Springer, Berlin.
- Schmitt M., Hasse H., Althaus K., Schoenmakers H., Goetze L., Moritz P., 2004. Synthesis of n-hexyl acetate by reactive distillation. *Chem. Eng. Process.*, 43, 397–409. DOI: 10.1016/S0255-2701(03)00124-7.
- Schoenmakers H., Besslin, B., 2003. Reactive and catalytic distillation from an industrial perspective. *Chem. Eng. Process.*, 42, 145–155. DOI: 10.1016/S0255-2701(02)00085-5.
- Schwefel H.-P., 1981. *Numerical optimisation of computer models*. 1st edition, Wiley-VCH, Chichester.
- Schwefel H.-P., 1995. *Evolution and optimum seeking*. 1st edition, Wiley-VCH, New York.
- Smith J.E., 2008. Self-adaptation in evolutionary algorithms for combinatorial optimisation. In: Cotta C., Sevaux M., Soerensen K. (Eds.), *Adaptive and multilevel metaheuristics*. 1st edition, Springer, Berlin, Heidelberg, 31–57.
- Stankiewicz A., 2003. Reactive separations for process intensification: an industrial perspective. *Chem. Eng. Process.*, 42, 137–144. DOI: 10.1016/S0255-2701(02)00084-3.
- Steinigeweg S., Gmehling J., Gmehling J., 2004. Transesterification processes by combination of reactive distillation and pervaporation. *Chem. Eng. Process.*, 43, 447–456. DOI: 10.1016/S0255-2701(03)00129-6.
- Sulzer Chemtech, 2004. Sulpak.
- Suman T., Srinivas S., Mahajani S.M., 2009. Entrainer based reactive distillation for esterification of ethylene glycol with acetic acid. *Ind. Eng. Chem. Res.*, 48, 9461–9470. DOI: 10.1021/ie801886q.
- Sundmacher K., Hoffmann U., 1996. Development of a new catalytic distillation process for fuel ethers via a detailed nonequilibrium model. *Chem. Eng. Sci.*, 51, 2359–2368. DOI: 10.1016/0009-2509(96)00092-9.
- Sundmacher K., Kienle A. (Eds.), 2003. *Reactive distillation. Status and Future Directions*. 1st edition, Wiley-VCH, Weinheim.
- Takeuchi T., Noguchi S., Morimoto H., Tobishima S.-I., 2010. Carbonate-modified siloxanes as solvents of electrolyte solutions for rechargeable lithium cells. *J. Power Sources*, 195, 580–587. DOI: 10.1016/j.jpowsour.2009.07.042.
- Talwalkar S., Mankar S., Katariya A., Aghalayam P., Ivanova M., Sundmacher K., Mahajani S., 2007. Selectivity engineering with reactive distillation for dimerization of C<sub>4</sub> olefins: experimental and theoretical studies. *Ind. Eng. Chem. Res.*, 46, 3024–3034. DOI: 10.1021/ie060860+.
- Taylor R., Krishna R., 2000. Modelling reactive distillation. *Chem. Eng. Sci.*, 55, 5183–5229. DOI: 10.1016/S0009-2509(00)00120-2.
- Thotla S., Agarwal V., Mahajani S.M., 2007. Aldol condensation of acetone with reactive distillation using water as a selectivity enhancer. *Ind. Eng. Chem. Res.*, 46, 8371–8379. DOI: 10.1021/ie061658+.
- Thotla S., Mahajani S.M., 2009. Conceptual design of reactive distillation for selectivity improvement in multiple reactant systems. *Chem. Eng. Res. Des.*, 87, 61–82. DOI: 10.1016/j.cherd.2008.07.003.
- Urselmann M., Barkmann S., Sand G., Engell S., 2011. A memetic algorithm for global optimisation in chemical process synthesis problems. *IEEE Trans. Evol. Comput.*, 15, 659–683. DOI: 10.1109/TEVC.2011.2150753.
- van Gerven T., Stankiewicz A., 2009. Structure, energy, synergy, time—the fundamentals of process intensification. *Ind. Eng. Chem. Res.*, 48, 2465–2474. DOI: 10.1021/ie801501y.
- Wei H.-Y., Rokhmah A., Handogo R., Chien I.-L., 2011. Design and control of reactive-distillation process for the production of diethyl carbonate via two consecutive transesterification reactions. *J. Process Control*, 21, 1193–1207. DOI: 10.1016/j.jprocont.2011.06.006.
- Zadeh L., 1963. Optimality and non-scalar-valued performance criteria. *IEEE Trans. Automat. Contr.*, 8, 59–60. DOI: 10.1109/TAC.1963.1105511.
- Zhang X., Zuo J., Jian C., 2010. Experimental isobaric vapour-liquid equilibrium for binary systems of ethyl methyl carbonate + methanol, + ethanol, + dimethyl carbonate, or + diethyl carbonate at 101.3 kPa. *J. Chem. Eng. Data*, 55, 4896–4902. DOI: 10.1021/je100494z.
- Zielinska I.N., Warmuzinski K., Richter J., 2006. Zeolite and other heterogeneous catalysts for the transesterification reaction of dimethyl carbonate with ethanol. *Catal. Today*, 114, 226–230. DOI: 10.1016/j.cattod.2006.01.001.

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## APPENDIX

In the present work, UNIQUAC equations were applied to take into account the nonideal behaviour of the liquid phase. In UNIQUAC equations, the size and volume of molecules are described by the volume parameter  $r_i$  and the area parameter  $q_i$ . Both pure component parameters were taken from the literature and are listed in Table A-1. To describe the composition and temperature dependence of the activity coefficient  $\gamma_i$ , the interaction parameter  $\tau_{ij}$  was considered to be temperature-dependent in the UNIQUAC model (see Eq. A-1).

$$\tau_{ij} = \exp(a_{ij} + b_{ij} / T) \quad (\text{A-1})$$

The coefficients of Eq. A-1,  $a_{ij}$  and  $b_{ij}$ , were obtained by regressing them to experimental vapour-liquid equilibrium data, which were available in the open literature for all binary mixtures. The resulting coefficients of Eq. A-1,  $a_{ij}$  and  $b_{ij}$ , are listed in Table A-2 and the corresponding values of  $R^2$ , the coefficient of determination, are provided to demonstrate that the description of the binary vapour-liquid equilibria by the UNIQUAC equations is excellent.

Table A-1. Pure-component volume parameter  $r_i$  and area parameter  $q_i$  used in the UNIQUAC model

Component	$r_i$	$q_i$	Reference
Methanol	1.431	1.432	Gmehling et al. (1977)
Ethanol	2.105	1.972	Gmehling et al. (1977)
Dimethyl carbonate	3.048	2.816	Gmehling and Onken (2002)
Ethyl methyl carbonate	3.781	3.388	Luo et al. (2000)
Diethyl carbonate	4.397	3.896	Gmehling and Onken (2002)

Table A-2. UNIQUAC binary interaction parameters  $a_{ij}$  and  $b_{ij}$  (see Eq. A-1). The corresponding values for the coefficient of determination,  $R^2$ , and the source publications for the experimental data are also included

Component 1	Component 2	$i$	$j$	$a_{ij}$	$b_{ij}$ (K)	$R^2$	Reference
Methanol	Ethanol	1	2	0.000	-48.990	0.9999	Gmehling et al. (1977)
		2	1	0.000	38.517		
Methanol	Dimethyl carbonate	1	2	-0.201	14.870	0.9999	Rodríguez et al. (2002)
		2	1	0.273	-306.550		
Methanol	Ethyl methyl carbonate	1	2	0.086	-38.822	0.9995	Zhang et al. (2010)
		2	1	-0.026	-278.229		
Methanol	Diethyl carbonate	1	2	-0.322	71.678	0.9987	Rodríguez et al. (2003)
		2	1	0.369	-376.829		
Ethanol	Dimethyl carbonate	1	2	0.000	-93.595	0.9999	Rodríguez et al. (2002)
		2	1	0.000	-81.760		
Ethanol	Ethyl methyl carbonate	1	2	0.156	-21.509	0.9996	Zhang et al. (2010)
		2	1	-0.091	-197.632		
Ethanol	Diethyl carbonate	1	2	-0.298	131.676	0.9987	Rodríguez et al. (2003)
		2	1	0.381	-365.987		
Dimethyl carbonate	Ethyl methyl carbonate	1	2	-0.230	30.426	0.9997	Zhang et al. (2010)
		2	1	-0.030	57.864		
Dimethyl carbonate	Diethyl carbonate	1	2	-1.523	57.293	0.9984	Luo et al. (2000)
		2	1	0.410	232.946		
Ethyl methyl carbonate	Diethyl carbonate	1	2	-0.333	195.435	0.9999	Zhang et al. (2010)
		2	1	0.378	-219.275		