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# Optimal design of intensified processes for DME synthesis

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## Keywords

Dimethyl ether, gas-phase reactor, reactive distillation, process design, process optimization

## Highlights

- Rigorous design and simulation of gas-phase and reactive distillation DME processes
- Reactive distillation is suitable for new DME plants due to lowest CapEx and OpEx
- Existing plants can be revamped to gas-phase reactor coupled with reactive distillation

## Abstract

Dimethyl ether (DME) is widely used as green aerosol propellant, precursor to other organic compounds, or as a clean fuel for diesel engines or in combustion cells. The classic method for producing DME is by dehydration of methanol in a catalytic gas-phase reactor, and purification in a direct sequence of two distillation columns. Reactive distillation (RD) is a much better alternative for DME synthesis, based on process intensification principles.

This paper presents the optimal design of novel DME processes based on reactive distillation, and makes a fair comparison with the classic reactor-separation-recycle process (for a plant capacity of 100 ktpy DME). The new RD processes were optimized in terms of minimizing the total annual costs, leading to savings of 30% in CapEx and 6% in energy requirements for the RD process. The results indicate that a RD column is recommended for new DME plants, while a combination of gas-phase reactor and RD is suitable for revamping existing plants.

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## 1 **1. Introduction**

2 Dimethyl ether (DME) has remarkable properties (e.g. non-toxic colorless gas, non-corrosive,  
3 non-carcinogenic, environmentally friendly) that make it usable as green aerosol propellant,  
4 as precursor to organic compounds, and as clean fuel for diesel engines or combustion cells  
5 (Muller and Hubsch, 2005). It is worth noting that DME market is estimated to worth 9.7  
6 billion USD by 2020 ([www.marketsandmarkets.com](http://www.marketsandmarkets.com)).

7 Many of the current industrial DME plants are based on the methanol dehydration route – in a  
8 conventional reactor-separation-recycle process (Kiss et al., 2007; Dimian et al., 2014) –  
9 whereas methanol can be produced from (bio-based) syngas or by CO<sub>2</sub> hydrogenation (Kiss et  
10 al., 2016). The chemical recycling of carbon dioxide to methanol and dimethyl ether has been  
11 advocated by Olah et al. (2009) and it plays a key role in a methanol economy.

12 Unexpectedly, there are only few references in literature related to the design and economic  
13 evaluation of an entire process for DME synthesis. Lei et al. (2011) discuss the economics of  
14 a process consisting of a fixed-bed reactor and two ordinary distillation columns.  
15 Nevertheless, the reactor is modeled as a simple Gibbs reactor where equilibrium is attained.

16 The recycle of unreacted methanol was not considered, neither the issues related to heating of  
17 the reactant, cooling the reactor effluent, or heat-integration. Bai et al (2013) presented the  
18 simulation of a process for DME synthesis by vapor phase methanol dehydration in a fixed-  
19 bed adiabatic reactor, with 1000 ktpy production rate. The simulation model is also compared  
20 to data acquired from a set of industrial production equipment with a capacity of 200 ktpy. An  
21 industrial solid acidic catalyst was used, and the kinetic model was developed by the same  
22 authors (Li et al, 2009). A follow-up paper (Bai et al., 2014) mentions a five-bed industrial  
23 reactor, operated adiabatically and provided with heat-exchangers for inter-stage cooling.

24 They also present detailed simulation results for a three-bed adiabatic reactor where inter-  
25 stage cooling is achieved by injecting (a fraction of) the fresh, reactor cold feed. Farsi et al.  
26 (2010) used a genetic algorithm to find the temperature distribution in a multi-tubular reactor  
27 which maximizes the DME production rate. Compared to the conventional adiabatic reactor,  
28 the methanol conversion increases from 81.9% to 85.75% which results in 4.3% increase of  
29 DME production rate. However, this is achieved at the cost of a more complex reactor. The  
30 authors also remark that the optimal temperature profile is difficult to be obtained in practice.

31 None of the above-mentioned papers (Bai et al., 2014, Farsi et al., 2010) discuss the positive  
32 impact that the more complex reactor setup has on the plant profitability. Han et al (2009)  
33 presented the simulation of a one-step process for DME production in a slurry reactor, from  
34 coal-based syngas (66.25 ktpy production rate). A simple CSTR model was used, after

1 verification on a set of experimental data obtained on a laboratory-scale reactor fed with 0.93  
2 mol/h syngas.

3 To increase the capacity of DME production, the chemical industry needs novel eco-efficient  
4 processes that can meet the growing market demand (Arcoumanis et al., 2008; Azizi et al.,  
5 2014). The suggested improvements of the methanol dehydration process followed a number  
6 of technologies reported in literature: fully thermally-coupled distillation columns (Petlyuk)  
7 or dividing-wall column replacing the direct distillation sequence (Kiss, 2013; Kiss and Ignat,  
8 2013); self-heat recuperation (Kansha et al., 2015); simultaneous synthesis and separation in a  
9 catalytic distillation process (An et al., 2004; Lei et al., 2011); catalytic cyclic distillation  
10 (Patrut et al., 2014); or reactive dividing-wall column (Kiss and Suszwalak, 2012). Additional  
11 DME technologies (e.g. coupled and dual type reactors, micro-reactors, membrane reactors,  
12 and spherical reactors), including the direct route from syngas, are also well described in the  
13 review paper of Azizi et al. (2014).

14 Among these technologies, reactive distillation (RD) seems to be the most promising (Azizi et  
15 al, 2014), being a proven process intensification method that effectively combines the reaction  
16 and separation into a single unit (Agrega et al., 1990). RD can considerably improve the  
17 performances of an equilibrium limited process, by pulling the conversion to completion (thus  
18 avoiding recycles), increasing selectivity and productivity, reducing the energy use, and  
19 overall reducing the CapEx and OpEx (Huss et al., 1999, Malone et al., 2003; Schoenmakers  
20 and Bessling, 2003; Sundmacher and Kienle, 2003; Harmsen, 2010; Kiss and Bildea, 2012).

21 This study is the first to provide the optimal design of novel DME processes based on reactive  
22 distillation, one process (single RD column) being most suitable for new DME plants, and  
23 another one (coupling a gas-phase reactor and a RD column) that is more appropriate for  
24 revamping existing DME plants based on gas-phase methanol dehydration. These novel  
25 process alternatives are optimized in term of minimum total annual costs (TAC) and  
26 compared to the classic reactor-separation-recycle process (at a capacity of 100 ktpy DME,  
27 over 99.99% purity), in terms of key performance indicators (e.g. CapEx, OpEx, and specific  
28 energy usage). Rigorous design and simulations were performed in Aspen Plus, including  
29 accurate LHHW kinetics for both the gas-phase and liquid-phase reactions as well as rigorous  
30 phase equilibrium calculations.

31

## 32 **2. Problem statement**

33 Due to the ever increasing demand in cheap chemicals and alternative fuels, the industry  
34 strives to deliver DME at even lower costs using the current plants (optimized and revamped)

1 or new plants based on process intensification technologies. Most of the DME technologies  
2 described in literature (Azizi et al., 2014) are hindered by the incomplete conversion of  
3 methanol which requires costly downstream processing, recovery and large recycle of  
4 methanol (up to 40% of the fresh methanol feed). To solve this problem, this study proposes  
5 DME process alternatives based on reactive distillation, which allows the complete  
6 conversion of methanol (and avoids recycle streams) at competitive costs.

### 7 8 **3. Simulation approach**

9 Rigorous simulations were performed in Aspen Plus for each of the process alternatives  
10 investigated in this study, considering a plant capacity of 100 ktpy DME. This section  
11 provides details on the thermodynamics and kinetic parameters, as well as the methodology  
12 used for the process optimization (i.e. minimization of the total annual costs) and economic  
13 evaluation (e.g. estimation of capital and operating expenditures).

#### 14 15 **3.1 Physical properties**

16 The non-ideality of the liquid phase was modeled using the UNIQUAC liquid activity model.  
17 The methanol-water and methanol-DME binary interaction parameters are available in the  
18 Aspen Plus database, while the water-DME binary interaction parameters were taken from the  
19 NIST database. The non-ideality of the vapor phase was modeled by the Redlich-Kwong  
20 equation of state. Redlich-Kwong EOS requires critical properties of the pure components,  
21 which are also available in the Aspen Plus database. The property model was also validated  
22 against experimental data reported in literature (Teodorescu and Rasmussen, 2001; Ihmels  
23 and Lemmon, 2007; Wu et al, 2011). Figure 1 shows the residue curves map (RCM) and the  
24 ternary map of the DME-methanol-water mixture (Kiss and Suszwalak, 2012). There are no  
25 azeotropes present in this system, but there is a small region where phase splitting is possible.

#### 26 27 **3.2 Reaction kinetics**

28 DME is formed in the reversible chemical reaction of methanol dehydration, either in gas-  
29 phase (catalyzed by  $\gamma$ -alumina) or in liquid-phase (catalyzed by ion exchange resins).



31  
32 *Gas-phase reaction.* The reaction rate of the gas phase methanol dehydration, on a  
33 commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, was described by the following kinetics. The apparent kinetic

1 parameters provided by Berčić and Levec (1993) were used (the original apparent rate  
 2 constant  $k_s$  was increased by a factor 100, in order to match the effectiveness factor presented  
 3 in the same paper). Other similar kinetics are reported in literature (Mollavali et al., 2008).

$$4 \quad r = \frac{k_s K_M^2 \left( y_M^2 - \frac{y_W y_D}{K_{eq}} \right)}{\left( 1 + 2\sqrt{K_M y_M} + K_W y_W \right)^4} \quad (2)$$

5 With the following constants:

$$6 \quad k_s = 3.30 \times 10^9 \exp(-10800/T), \text{ kmol}/(\text{kg}\cdot\text{h})$$

$$7 \quad K_M = 0.72 \times 10^{-2} \exp(830/T), \text{ dimensionless}$$

$$8 \quad K_W = 0.45 \times 10^{-2} \exp(1130/T), \text{ dimensionless}$$

9 The equilibrium constant  $K_{eq}$  was calculated (by Aspen Plus) from Gibbs free energies.

10

11 *Liquid-phase reaction.* The reaction rate of the liquid phase methanol dehydration on  
 12 Amberlyst-35 was described by the following rate equation – using the kinetic parameters  
 13 from Hosseninejad et al. (2012):

$$14 \quad r = \frac{k_s}{\left( 1 + \frac{K_W c_W}{K_M c_M} \right)^2} \left( 1 - \frac{1}{K_{eq}} \frac{c_D c_W}{c_M^2} \right) \quad (3)$$

15 With the following constants:

$$16 \quad k_s = 6.12 \times 10^9 \exp(-11793/T), \text{ kmol} / (\text{kg}\cdot\text{s})$$

$$17 \quad K_W/K_M = \exp(-6.46 + 2964.0/T)$$

18  $K_{eq} = \exp(-2.6305 + 2787/T)$ , regressed from equilibrium constant ( $K_{eq}$ ) values calculated by  
 19 Aspen Plus from Gibbs free energies.

20

### 21 **3.3 Optimization and economics**

22 Optimizing a chemical process is usually a mixed-integer nonlinear problem that is non-  
 23 convex and likely to have multiple locally optimal solutions. Hence a guarantee of  
 24 convergence to the globally optimal solution is not possible for non-convex problems. More  
 25 details about the decision variables, constrains and solution method are provided later, within  
 26 the appropriate context. In this work, each process design is optimized using the minimization  
 27 of the total annual cost (TAC) as objective function:

$$28 \quad TAC = OpEx + \frac{CapEx}{\text{payback period}} \quad (4)$$

1 A payback period of 3 years was used, and a running time of 8000 hours/year was considered.  
 2 The following heating and cooling costs were taken into account: high-pressure (HP) steam  
 3 (42 bar, 254 °C, \$9.88/GJ), medium-pressure (MP) steam (11 bar, 184 °C, \$8.22/GJ), low-  
 4 pressure (LP) steam (6 bar, 160 °C, \$7.78/GJ), and cooling water (\$0.72/GJ). These costs of  
 5 utilities are typical for a US plant (Luyben, 2011), but they might differ for other locations.  
 6 The total investment costs (CapEx) include the reactor, all heat exchangers, and distillation  
 7 columns. The cost of the heat exchangers (reboiler, condenser, FEHE, steam generator,  
 8 cooler) are given by (Turton et al., 2009):

$$9 \quad C_{HEX} (US\$) = (M \& S / 280) \cdot (474.7 \cdot A^{0.65}) (2.29 + F_m (F_d + F_p)) \quad (5)$$

$$10 \quad C_{furnace} (US\$) = (M \& S / 280) \cdot (15668 \cdot Q^{0.85}) (1.27 + F_c) \quad (6)$$

11 where  $M\&S$  is the Marshall & Swift equipment cost index ( $M\&S=1536.5$  in 2012),  $A$  is the  
 12 area ( $m^2$ ),  $F_m = 1$  (carbon steel),  $F_d = 0.8$  (fixed-tube),  $F_p = 0$  (less than 20 bar). A heat  
 13 transfer coefficient  $U=0.5$  kW/ $m^2$ /K was assumed to calculate the heat transfer area. For the  
 14 reboilers, the design factor was taken as  $F_d = 1.35$ . For the furnace,  $Q$  is the duty (in MW),  
 15 while the correction factor was taken as  $F_c = 1$  (process heater, carbon steel, design pressure  
 16 less than 40 bar).

17 The distillation columns diameter ( $D$ ) were obtained by the tray sizing utility from Aspen  
 18 Plus, while the height was evaluated from the number of trays ( $NT$ ), as:  $H = 0.6 \cdot (NT - 1) + 2$   
 19 (m). Afterwards, the cost of the columns shell was calculated as:

$$20 \quad C_{shell} (US\$) = (M \& S / 280) \cdot (957.9 \cdot D^{1.066} \cdot H^{0.82}) \cdot (2.18 + F_c) \quad (7)$$

21 The cost of the trays was given by (Turton et al., 2009):

$$22 \quad C_{trays} (US\$) = NT \cdot (M \& S / 280) \cdot 97.2 \cdot D^{1.55} \cdot (F_t + F_m) \quad (8)$$

23 with  $F_t = 0$  (sieve trays) and  $F_m = 1$  (carbon steel)

24 where  $F_c = F_m \cdot F_p$ ,  $F_m = 1$  (carbon steel) and  $F_p = 1 + 0.0074 \cdot (P - 3.48) + 0.00023 \cdot (P - 3.48)^2$

25  
 26 The price of the structured packing (KATAPAK-SP 11) was taken as 10,000 \$/ $m^3$ . The  
 27 relationship (7) was also used to estimate the cost of the tubular reactor. For the solid acid  
 28 catalyst (Amberlyst-35 ion exchange resin, with a bulk density of 560 kg/ $m^3$ ) and the gas-  
 29 phase catalyst ( $\gamma$ -alumina, bulk density 882 kg/ $m^3$ , particle size 3 mm), a purchased cost of 10  
 30 \$/kg was considered. Clearly, the price of catalyst differs per country and manufacturer.

31

## 1 **4. Results and discussion**

2 This section provides the simulation results for the three DME process options considered:  
3 reactor-separation-recycle (R-S-R) process, single step process using a reactive distillation  
4 column, and combined gas-phase reactor and reactive distillation process.

5

### 6 **4.1 Reactor-separator-recycle process**

7 In the conventional R-S-R process, methanol is dehydrated over a  $\gamma$ -alumina catalyst (or  
8 HZSM-5, silica-alumina, phosphorous-alumina and fluorinated-alumina) to produce DME.

9 The fixed-bed gas-phase reactor is operated at 250-400°C and pressure up to 20 bars. Due to  
10 incomplete conversion, a direct sequence of two distillation columns is required to deliver  
11 high-purity (min. 99.99 %wt) DME (Muller and Hubsch, 2005; Kiss and Ignat, 2013).

12 Figure 2 shows the process flowsheet, mass balance and the key design parameters of the  
13 reactor-separation-recycle process for DME production. The fresh methanol feed is mixed  
14 with the recycled methanol stream and fed via a feed-effluent heat exchanger (FEHE) to a  
15 furnace, which vaporizes the whole stream. Methanol vapor is converted in the reactor to  
16 DME and water, but the conversion is incomplete. The hot reactor outlet stream is used in  
17 FEHE to pre-heat the feed to the reactor, and then the remaining heat of the hot stream is used  
18 for steam generation (which can be used for the reboiler of methanol recovery column). The  
19 outlet of the steam generator is fed directly, as vapor, to the DME distillation column (COL-1).  
20 Note that further cooling to liquid at boiling point (about 64 °C) increases the TAC, as an  
21 additional heat exchanger is needed and transferring the heat to cooling water increases the  
22 duty required for DME separation. In COL-1, the DME is separated as top distillate, while the  
23 bottom product (mixture of methanol and water) is fed to the methanol recovery column  
24 (COL-2), which separates methanol as distillate (a stream that is recycled in the process) and  
25 water by-product as bottom stream.

26 For the conventional process, the choice of the reactor is a major design decision, as it  
27 determines the achievable conversion. In general, approaching the chemical equilibrium  
28 condition has a beneficial effect on the TAC, as the cost reduction of the separation section  
29 (CapEx and OpEx) overcome the expense of using more catalyst.

30 When a single-bed adiabatic reactor is used, the design decisions concern the reactor size  
31 (diameter and length) and the reactor-inlet temperature. The diameter was calculated by  
32 imposing a fluid velocity  $u = 0.25$  m/s, which is in line with the reported value of an industrial  
33 DME reactor (Bai et al, 2013). Note that a high velocity ( $> 2$  m/s) results in (unpractical) high  
34 pressure drop while a lower velocity decreases the mass transfer rate from the fluid to the



1 solid catalyst particle. Concerning the reactor length, a longer reactor (more catalyst) leads to  
2 higher conversion and thus reduces the separation costs, but pressure drop increases and the  
3 reactor is more difficult to build and operate. A higher feed temperature increases the reaction  
4 rate and therefore reduces the amount of catalyst required to achieve a certain conversion. On  
5 the other hand, more heat is required and the achievable conversion is reduced due to the  
6 exothermal nature of the chemical reaction. Moreover, the temperature along the reactor bed  
7 is increased, with negative effect on catalyst stability. Figure 3 presents the TAC versus inlet  
8 temperature, for reactors with different lengths. For each reactor, the optimal operating point  
9 (minimum plant TAC) is marked, together with the values of the total annual cost,  $TAC^*$ , total  
10 investment cost  $TIC^*$ , total operating cost  $TOC^*$ , pressure drop along the reactor,  $\Delta P$ , and  
11 maximum temperature along the reactor bed,  $T_{out}$ . It can be observed that the reactor leading  
12 to minimum TAC while fulfilling the constraint of outlet temperature below 400 °C (when the  
13 catalyst starts to deactivate) has the 12 m length, being fed at 275 °C. This will be considered  
14 for further comparison with other design alternatives.

15 Figure 4 presents lines of constant reaction rate in the temperature – conversion plane. The  
16 line of maximum reaction rate (at a given conversion) is represented by the dashed line. Also,  
17 the figure shows the reaction trajectories corresponding to reactors of length 8 m, 12 m and 16  
18 m, fed at the optimum temperature. It can be noticed that all the optimal reactors approach the  
19 equilibrium, therefore the reduction of separation costs exceeds the cost of using more  
20 catalysts.

21 While evaluating the TAC shown in Figure 3, the performance of the distillation columns was  
22 specified in terms of distillate purity (99.99 %wt DME, COL-1) and bottoms purity (>99.95  
23 %wt water, COL-2). The usual design condition of  $R = 1.2 R_{min}$  (Luyben, 2011) was used,  
24 while the location of the feed tray was chosen such that the minimum reboiler duty is  
25 achieved. The specification for the methanol recycle purity (in the range 0.95 %wt to 0.999  
26 %wt) had little influence on the optimal reactor design and minimum TAC value. The DME  
27 column (COL-1) was operated at 10 bar, which allows use of cooling water in the condenser.

28 The FEHE increases the temperature of the reactor feed stream up to 140 °C, by using the  
29 reactor effluent as heat source. Note that the amount of heat that can be recovered in the  
30 FEHE is limited by the temperature crossover which occurs when higher outlet temperature of  
31 the cold stream is specified (Figure 5).

32 Table 1 and Table 2 list the simulation results of the R-S-R process for DME production,  
33 while Table 3 provides a summary of the economic results. Note that the furnace contributes  
34 by 29% to CapEx and 61% to OpEx, so heat-recovery (using FEHE, steam generation and

1 vapour feed to the DME column) plays an important role in the process. The specific energy  
2 requirements are 2.58 MJ/kg (714 kWh/ton) DME.

#### 4 **4.2 Reactive distillation process**

5 RD conveniently combines reaction and separation in a single unit that can drive conversion  
6 to completion by continuously removing the products from the system. In such processes,  
7 designing a RD column at the maximum driving force results in an optimal design in terms of  
8 controllability and operability, which is less sensitive to disturbances in the feed and has the  
9 inherent ability to reject disturbances (Mansouri et al., 2015).

10 As shown in Figure 6, methanol is fed at the top of the reactive zone in the RD column (on  
11 stage 9). The reaction takes place in the reactive zone where the solid acid catalyst is placed  
12 (stages 9-42). DME is the lightest component in the system hence removed as top distillate,  
13 while water is the heaviest component hence removed as bottoms. Unlike the gas-phase  
14 reaction, the dehydration of methanol in liquid phase is catalyzed by thermally stable resins,  
15 such as Amberlyst-35 which has high activity and selectivity at temperatures up to 150 °C.

16 The design of RD processes can be performed using single and multi-objective optimization  
17 approaches (Segovia-Hernandez et al., 2015). The optimal design of the RD process (and the  
18 next one using reactive distillation) is a mixed-integer nonlinear problem (MINLP). Such  
19 problems are intrinsically very difficult to solve, and the solution time increases rapidly with  
20 the number of variables and constraints.

21 The decision variables used in the optimization are the following:

- 22 • Discrete (integers): number of stages ( $NT$ ), feed stage ( $NF$ ), reactive stages ( $NR_1 - NR_2$ )
- 23 • Continuous (real numbers): reflux ratio ( $RR$ ), pressure ( $P$ ), amount of catalyst / tray ( $m_{cat}$ )

24 The optimization considers the following constraints:

- 25 • Distillate purity: 99.99 % wt DME
- 26 • Bottoms purity: exceeding 99.95 % wt
- 27 • Temperature on the reactive stages: below 150 °C (to avoid catalyst deactivation)
- 28 • Catalyst must fit into the available space (no more than 20% of the packing volume)

29 Note that the optimal steady state operating point is often defined by the intersection of active  
30 constraints (Kookos and Perkins, 2016). This well-established feature of chemical processes  
31 is neatly exploited to simplify the solution of the optimization problem. Thus, the RD column  
32 for DME synthesis has the following features, confirmed by several sensitivity analysis runs:

- 33 • When the distillate rate is set to half of the feed (based on reaction stoichiometry), due to

1 the relative volatilities of the species involved in the process, methanol is equally  
2 distributed between the distillate and the product streams. Therefore, achieving 99.99 %wt  
3 distillate purity (DME) by manipulating the reflux ratio also ensures that the purity of the  
4 bottoms stream (water) exceeds the 99.95 %wt requirement.

- 5 • The operating costs (OpEx) represent more than 75% of the TAC. The main contributions  
6 to the capital costs (CapEx) are the condenser, reboiler, column shell and structured  
7 packing, with the catalyst representing less than 3%. For this reason, increasing the  
8 amount of catalyst per theoretical stage invariably results in a lower value of the TAC, as  
9 the reduction of the other costs clearly outweighs the cost of catalyst. However, the  
10 amount of catalyst is limited to 20% of the available volume (Götze et al., 2001).
- 11 • Increasing the operating pressure leads to higher temperature along the RD column. This  
12 results in faster reaction rates and, in turn, to lower TAC due to reduced effort necessary  
13 to achieve the separation. Therefore, the optimal pressure leads to the highest allowable  
14 temperature in the reactive section.

15 Based on these observations, the following optimization strategy is employed. In Aspen Plus,  
16 set the discrete decision variables: number of stages, feed stage, and reactive stages. The  
17 distillate molar rate is set to half of the feed, according to reaction stoichiometry. By means of  
18 *Design Specification* blocks, the continuous decision variables (reflux ratio, pressure, and  
19 amount of catalyst on each tray) are adjusted such that the constraints are fulfilled (distillate  
20 purity 99.99 %wt DME; temperature on reactive stages < 150 °C; catalyst fits into the  
21 available space of 20% of the packing volume). Due to mass balance and high purity of the  
22 distillate, the purity of the bottoms stream always exceeds the 99.95 %wt requirement. The  
23 simulation is run and the value of the TAC is obtained. Afterwards the discrete variables are  
24 adjusted, and new runs are performed, until the minimum TAC is obtained. In this work, the  
25 optimal values of the discrete variables are found using the genetic algorithm implemented in  
26 Matlab by means of the *ga* function. The user-provided Matlab objective function uses the  
27 COM interface to communicate with Aspen Plus: sends to Aspen Plus the values of the  
28 discrete decision variables, requests the simulation run and checks the convergence. After a  
29 successful run, the objective function (TAC, calculated in Aspen Plus by a FORTRAN  
30 *Calculator* block) and the continuous decision variables (obtained by the *Design Specification*  
31 blocks) are retrieved and saved in an Excel file together with the discrete decision variables.  
32 Then, the value of the objective function is passed to the *ga* function, which performs a new  
33 iteration. If Aspen Plus simulation does not converge, the simulation is re-initialized and a  
34 new run is attempted. If this also fails, a large value is returned to *ga* as the value of the

1 objective function. During an initial run, rather large ranges of the discrete variables were  
2 assumed and many Aspen Plus simulations were unsuccessful. After a better estimation of the  
3 optimum, the ranges were restricted as follows: feed tray: 7...12; first reactive stage: 7...12;  
4 last reactive stage 30...50; total number of stages: 45 ... 60. In this case, more than 95% of  
5 the simulations were successful. The progress of the optimization run is shown in Figure 7.  
6 Figure 6 also shows the process flowsheet, mass balance and the key operating parameters,  
7 while Table 4 provides the optimal design parameters of the RD column for DME production.  
8 The operating pressure (11.36 bar) leads to reactive stages temperature in the range 130-150  
9 °C. The amount of catalyst (193.2 kg/stage) occupies 20% of the stage volume, this being in  
10 line with the recommendations for KATAPAK packing (Götze et al., 2001). The reflux ratio,  
11 (6.174 kmol/kmol) ensures the required purity. Along the reactive stages, the liquid-phase  
12 methanol mole fraction exceeds 80%, which leads to a large reaction rate. For convenience,  
13 Figure 8 plots the temperature and reaction rate profiles while Figure 9 shows the liquid  
14 composition profiles along the RD column. Remarkable, for the RD process, the CapEx is  
15 only 2395 k\$, the OpEx is 2604 k\$/year, and the specific energy requirements are 2.43 MJ/kg  
16 (672.5 kWh/t) DME.

17

### 18 **4.3 Combined gas-phase reactor and reactive distillation**

19 The main idea of the combined process is to use only the reaction section of existing R-S-R  
20 processes for DME production, and include a reactive distillation column in the downstream  
21 processing, as shown in Figure 10. This allows complete reactant conversion and avoids the  
22 need of recycling. The reactor diameter decreases, but the effect on the TAC is small.  
23 However, it should be remarked that the gas-phase reactor of existing DME plants can process  
24 more fresh methanol (for example, the R-S-R process illustrated in the previous section could  
25 process **Figure 2** 748 kmol/hr instead of 546 kmol/hr). The methanol conversion is eventually  
26 driven to completion by the RD column. As the feed to the downstream processing section is  
27 not pure methanol (as in the single step RD process), but a ternary mixture (DME, methanol  
28 and water from the gas-phase reactor), an additional unit is necessary. Because water has the  
29 highest boiling point (and therefore in the RDC column will remain in the liquid phase) and  
30 has a detrimental effect on the reaction rate (see equation 3), this component is removed in the  
31 first distillation column. The water column was designed for 99% water recovery, at 99.97  
32 %wt purity. The methanol – DME mixture is fed above the reactive section of the RDC.  
33 In the RD column, the amounts of catalyst (67 kg/stage), is the maximum occupying 20% of  
34 the available space. Despite the higher methanol liquid phase concentration, the reaction rate

1 is lower compared to the single RD Column process due to less catalyst. Along the reactive  
2 stages, the temperature is in the range 134-147 °C. Figure 11 and Figure 12 present  
3 temperature, reaction rate and composition profiles along the RD column. Table 5 and Table 6  
4 list the simulation results of the combined process for DME production, while Table 7  
5 provides a summary of the economic results. For the same production capacity (100 ktpy) the  
6 cost of the reaction section is lower as compared to the classic R-S-R process due to the  
7 absence of the methanol recycle. However, the downstream processing section is somewhat  
8 more expensive than the classic direct distillation sequence, as the reaction must also be  
9 carried out together with the separation. Moreover, the reactor outlet is not fed as vapor to the  
10 RD column (due to the reaction taking place in liquid phase) but as saturated liquid  
11 (condensed in the prefractionator). As a consequence, the key economic indicators are slightly  
12 increased: CapEx is 3437 k\$, OpEx is 3152 k\$/year and the specific energy requirements are  
13 2.905 MJ/kg (807 kWh/ton) DME. Nonetheless, the key advantage of this process alternative  
14 is that due to the elimination of the methanol recycle, the production capacity could be  
15 increased by a factor equal to the reverse of the methanol conversion ( $1 / X_{\text{MeOH}}$ ).

16

## 17 **5. Process comparison**

18 The economic results are summarized for all cases in Table 3 (R-S-R process alternatives),  
19 Table 4 (single step process in RD column) and Table 7 (combined process). Based on these  
20 figures, it is clear that for a new DME plant the single step process using a reactive distillation  
21 column is the best option with the lowest CapEx (about 70% of the classic R-S-R process)  
22 and similar OpEx, with a reduction of 6% in the specific energy requirements.

23 However, in case of increasing the capacity of an existing DME plant, it would be cheaper to  
24 just revamp the plant by keeping the whole reaction section and reuse the columns of the  
25 direct distillation sequence to separate water (first column) and convert the remaining MeOH  
26 to DME (second column, reactive distillation). By doing so, the additional investment is  
27 minimized and the TAC reduced in spite of the slight increase in OpEx. Another key  
28 advantage of the combined process is possibility to significantly increase the plant capacity  
29 due to the absence of the methanol recycle.

30

## 31 **6. Conclusions**

32 The rigorous process simulations showed that the novel process alternatives based on reactive  
33 distillation can significantly improve the classic reactor-separator-recycle process for DME  
34 production. Based on the results presented here, the following conclusions can be drawn:

- 1       • The classic reactor-separator-recycle DME process could be improved by feeding the  
2       reactor outlet as vapor to the direct distillation sequence (about 8% savings in TAC).
- 3       • The single step process using a reactive distillation column is the most promising for  
4       new DME plants due to the lowest CapEx (2395 k\$) and OpEx (2604 k\$/year) - for  
5       100 ktpy plant capacity - as well as specific energy requirements (2.43 MJ/kg DME).
- 6       • The combined process (gas-phase reactor + reactive distillation) is not recommended  
7       for new plants (due to higher costs than the single step RD process), but it is suitable  
8       for revamping existing DME plants. With only a minor additional investment, the  
9       plant capacity can be significantly increased by having complete methanol conversion  
10      and no recycles, thus allowing a higher processing capacity of the fresh methanol feed.

## 12 **Acknowledgement**

13 Financial support of the European Commission through the European Regional Development  
14 Fund and of the Romanian state budget, under the grant agreement 155/25.11.2016 (Project  
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1 **Tables**

2

3 **Table 1.** Simulation results for the reactor-separator-recycle process for DME production  
 4 (100 ktpy): reaction system (without downstream processing)

5

<b>Parameter / unit</b>	<b>Value</b>
<b>Reactor</b>	
Length / [m]	12
Diameter / [m]	1.89
CapEx [k\$]	754.48
<b>FEHE</b>	
Area / [m]	12.32
Duty / [MW]Tab	2.29
CapEx [k\$]	41.18
<b>Furnace</b>	
Duty [MW]	6.88
CapEx / [k\$]	1006
OpEx / [k\$/year]	1983.7
<b>Steam generator</b>	
Duty / [MW]	0.576
Area / [m <sup>2</sup> ]	33.3
CapEx / [k\$]	104.1
OpEx / [k\$/year]	-129.21

6

7

1 **Table 2.** Simulation results for the reactor-separator-recycle process for DME production  
 2 (100 ktpy): downstream processing (direct distillation sequence)

3

	<b>DME Column</b>	<b>Methanol Column</b>
<b>Feed condition</b>		
Feed rate / [kmol/h]	667.25	394.25
Feed temperature / [°C]	170.0	86.5
<b>Design data</b>		
Number of stages, NT	18	30
Feed stage, NF	10	21
Diameter / [m]	1.68	1.16
Height / [m]	11.6	18.8
Reboiler area / [m <sup>2</sup> ]	44.5	77.0
Condenser area / [m <sup>2</sup> ]	681.1	144.7
<b>Operating data</b>		
Distillate rate / [kmol/h]	273	121.27
Bottoms rate / [kmol/h]	394.3	273
Reflux ratio	3.94	1.37
Reboiler duty / [MW]	0.625	2.044
Condenser duty / [MW]	6.45	2.82
Condenser pressure / [bar]	10	1
Distillate purity / [% wt]	99.99	99.95
Bottoms purity / [% wt]	-	99.98
<b>Economic data</b>		
CapEx / [k\$]	911.4	601.0
Condenser / [k\$]	558.9	204.2
Reboiler / [k\$]	111.7	159.2
Column shell / [k\$]	221.6	218.2
Trays / [k\$]	19.2	18.9
OpEx / [k\$/year]	282.2	516.6
Cooling / [k\$/year]	133.9	58.5
Heating (HP steam) / [k\$/year]	148.2	458.1
<b>TAC / [k\$/year]</b>	<b>586.0</b>	<b>716.9</b>

4

5

1

2 **Table 3.** Summary of economic results for the R-S-R process for DME production (100 ktpy)

	<b>CapEx / [k\$]</b>	<b>OpEx / [k\$/year]</b>	<b>TAC / [k\$/year]</b>
Reactor	754.5	-	251.5
FEHE	41.2	-	13.7
Furnace	1006.4	1983.7	2319.2
Steam generator	104.1	-129.2	-94.5
DME column	910.8	281.9	585.5
Methanol column	600.6	516	716.2
<b>TOTAL</b>	<b>3417.6</b>	<b>2652.4</b>	<b>3791.6</b>

3

4

1

2 **Table 4.** Optimal design parameters of a RD column for DME production (100 ktpy)

<b>Parameter / unit</b>	<b>Value</b>
<b>Design data</b>	
Number of stages, NT	54
Feed stage, NF	9
Reactive stages, NR <sub>1</sub> – NR <sub>2</sub>	9 - 42
HETP / [m]	0.5
Amount of catalyst / [kg/stage]	193.2
Catalyst volumetric fraction	0.2
Diameter / [m]	2.1
Height / [m]	28.0
Reboiler area / [m <sup>2</sup> ]	248.8
Condenser area / [m <sup>2</sup> ]	755.0
Feed preheater / [m <sup>2</sup> ]	132.3
<b>Operating data</b>	
Feed rate / [kmol/h]	546
Feed temperature / [°C]	85.4
Distillate rate / [kmol/h]	273
Bottoms rate / [kmol/h]	273
Reflux ratio	6.177
Reboiler duty / [MW]	8.485
Condenser duty / [MW]	9.148
Feed preheater / [MW]	0.943
Condenser pressure / [bar]	11.36
Distillate purity / [% wt DME]	99.99
Bottoms purity / [% wt water]	99.97
<b>Economic data</b>	
CapEx / [k\$]	2394.9
Condenser / [k\$]	597.6
Reboiler / [k\$]	342.2
Column shell / [k\$]	578.4
Packing / [k\$]	586.5
Catalyst / [k\$]	65.7
Trays / [k\$]	31.9
Feed pre-heater	192.6
OpEx / [k\$/year]	2604.2
Cooling / [k\$/year]	189.7
Heating (HP steam) / [k\$/year]	2414.5
<b>TAC / [k\$/year]</b>	<b>3402.5</b>

3

4

1 **Table 5.** Simulation results for the combined gas-phase reactor and reactive distillation  
 2 process for DME production (100 ktpy): gas-phase reactor section

<b>Parameter / unit</b>	<b>Value</b>
<b>Reactor</b>	
Length / [m]	12
Diameter / [m]	1.71
CapEx [k\$]	231.8
<b>FEHE</b>	
Area / [m]	11.8
Duty / [MW]	1.981
CapEx [k\$]	7.65
<b>Furnace</b>	
Duty [MW]	5.63
CapEx / [k\$]	848.66
OpEx / [k\$/year]	1671.55
<b>Steam generator</b>	
Duty / [MW]	0.366
Area / [m <sup>2</sup> ]	25.1
CapEx [k\$]	86.54
OpEx [k\$/year]	-82.08

3

4

1 **Table 6.** Simulation results for the combined gas-phase reactor and reactive distillation  
 2 process for DME production (100 ktpy): downstream processing section

<b>Parameter / unit</b>	<b>Water-column</b>	<b>RD column</b>
<b>Feed condition</b>		
Feed rate / [kmol/h]	546	324.8
Feed temperature / [°C]	164.2	66.6
<b>Design data</b>		
Number of stages, NT	18	35
Feed stage, NF	9	8
Reactive stages	-	8 - 25
Diameter / [m]		1.25
Height / [m]	1.38	21.8
Reboiler area / [m <sup>2</sup> ]	112	90.8
Condenser area / [m <sup>2</sup> ]	1066	386.4
Catalyst / [kg/stage]	-	67
Catalyst volumetric fraction [%]	-	0.2
<b>Operating data</b>		
Distillate rate / [kmol/h]	324.8	273
Bottoms rate / [kmol/h]	221.2	51.8
Reflux ratio	1.867	1.937
Reboiler duty / [MW]	1.727	3.159
Condenser duty / [MW]	7.118	3.822
Condenser pressure / [bar]	5	10.2
Distillate purity / [% wt]	0.003 (Water),	0.9999 (DME)
Bottoms purity / [% wt]	0.9997 (Water)	0.9997 (Water)
<b>Economic data</b>		
CapEx / [k\$]	1143.8	956.7
Condenser / [k\$]	747.9	386.8
Reboiler / [k\$]	203.6	177.8
Column shell / [k\$]	177.5	270.2
Trays / [k\$]	14.8	13.3
Packing / [k\$]	-	108.6
OpEx / [k\$/year]	556.6	1006.7
Cooling / [k\$/year]	147.6	79.3
Heating (HP steam) / [k\$/year]	409.0	927.4
<b>TAC / [k\$/year]</b>	<b>936.8</b>	<b>1325.6</b>

3

4

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1 **Table 7.** Summary of economic results for the combined gas-phase reactor and reactive  
 2 distillation process for DME production (100 ktpy)

	<b>CAPEX / [k\$]</b>	<b>OPEX / [k\$/year]</b>	<b>TAC / [k\$/year]</b>
Reactor	231.8	-	77.3
FEHE	7.65	-	2.55
Furnace	848.67	1671.55	1954.44
Steam generator	86.54	-82.08	-53.23
Water column	936.8	556.6	868.86
RD Column	1325.6	1006.7	1448.56
<b>TOTAL</b>	<b>3437.06</b>	<b>3152.77</b>	<b>4298.4</b>

3

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5



1 **Figure captions** (auto-updated)

2

3 **Figure 1.** Residue curve map and ternary diagram of the mixture DME-MeOH-H<sub>2</sub>O at 10 bar

4

5 **Figure 2.** Reactor-separation-recycle process for DME production

6

7 **Figure 3.** TAC vs reactor-inlet temperature, for reactors with various lengths. Total annual  
8 cost, pressure drop and reactor-outlet temperature are indicated, for each optimal point.

9

10 **Figure 4.** Methanol conversion versus temperature, at fixed reaction rate.

11

12 **Figure 5.** T–Q curve of the feed-effluent heat exchanger (FEHE), for two different values of  
13 the cold stream outlet temperature.

14

15 **Figure 6.** Single step process using a reactive distillation column for DME production

16

17 **Figure 7.** Progress of the RDC optimization

18

19 **Figure 8.** Temperature and reaction rate profile along the RD column

20

21 **Figure 9.** Liquid (continuous line) and vapor (dashed line) composition profiles along the RD  
22 column

23

24 **Figure 10.** Combined gas-phase reactor and reactive distillation process for DME production

25

26 **Figure 11.** Temperature and reaction rate profiles along the RD column, in the combined gas-  
27 phase reactor and RDC process

28

29 **Figure 12.** Liquid (continuous line) and vapor (dashed line) composition profiles along the  
30 RD column, in the combined gas-phase reactor and RDC process

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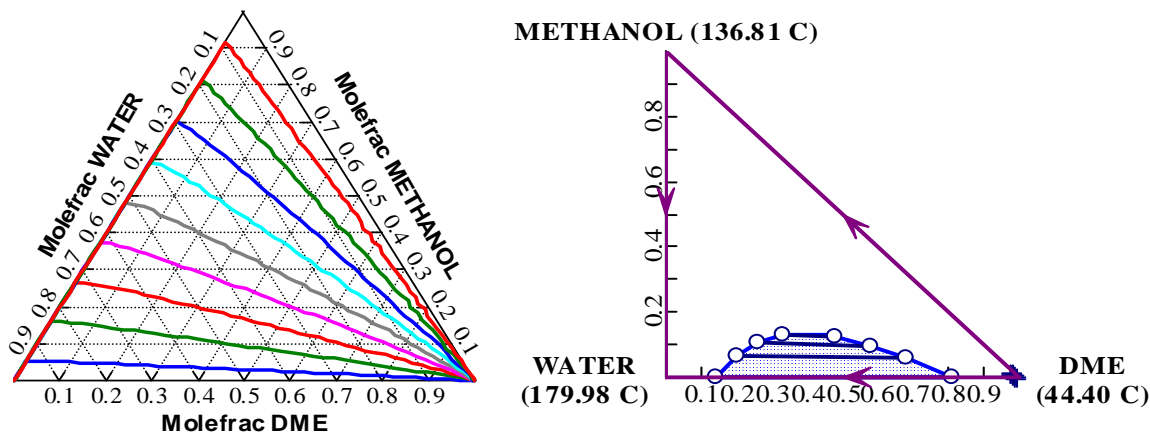


Figure 1. Residue curve map and ternary diagram of the mixture DME-MeOH-H<sub>2</sub>O at 10 bar

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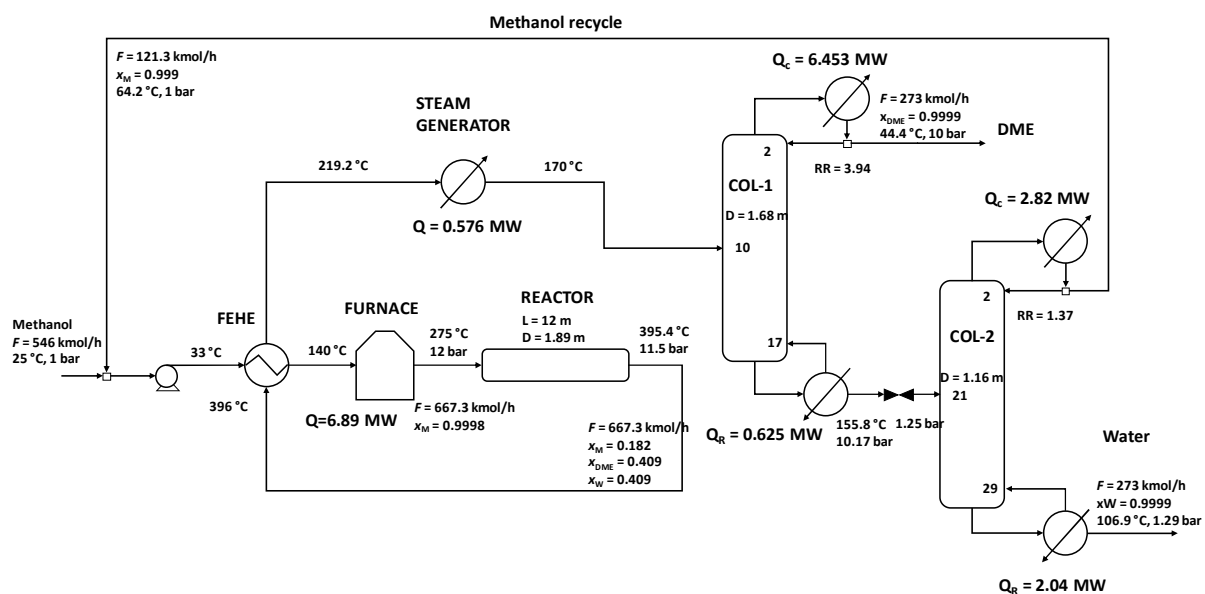
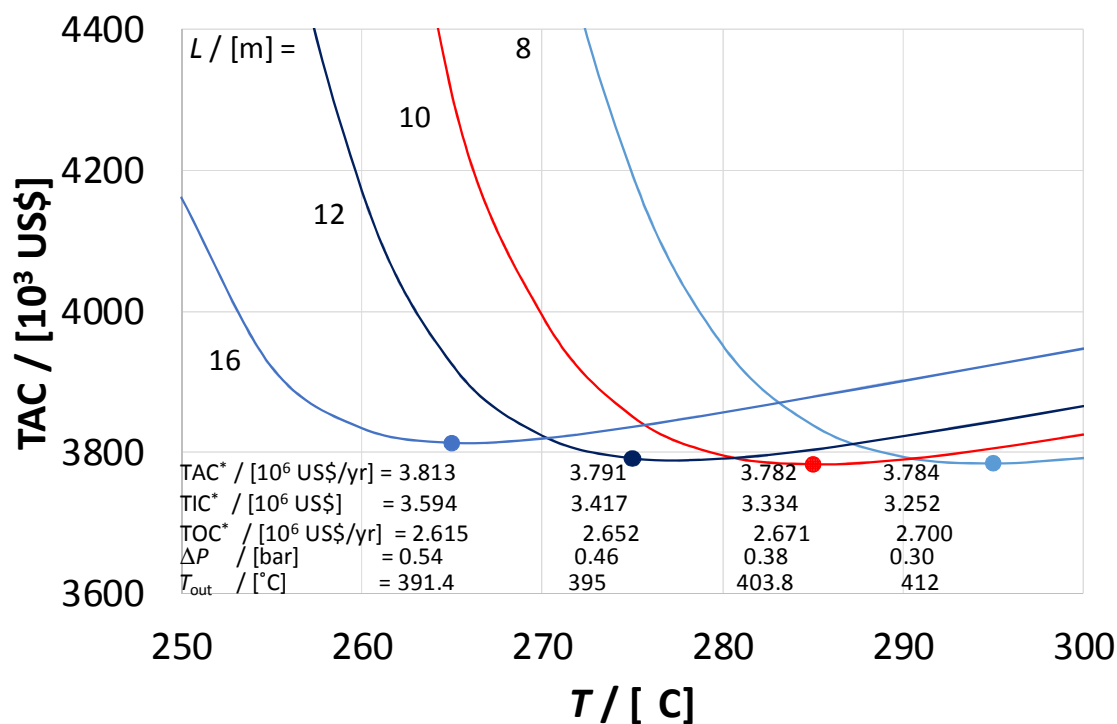
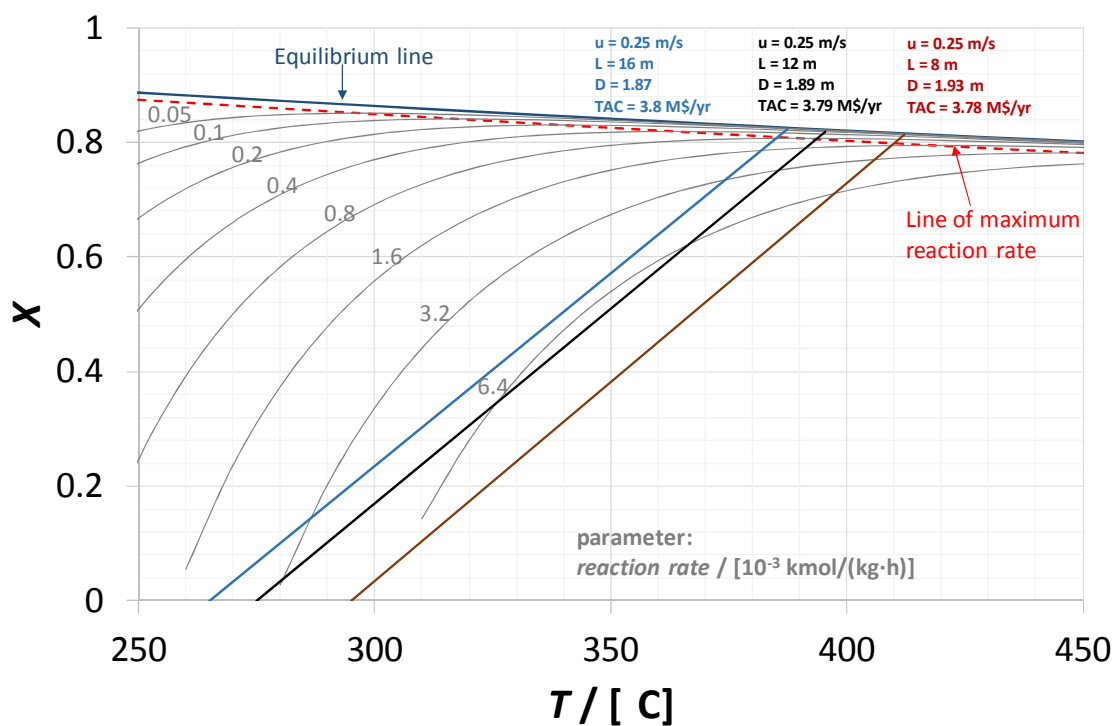


Figure 2. Reactor-separation-recycle process for DME production

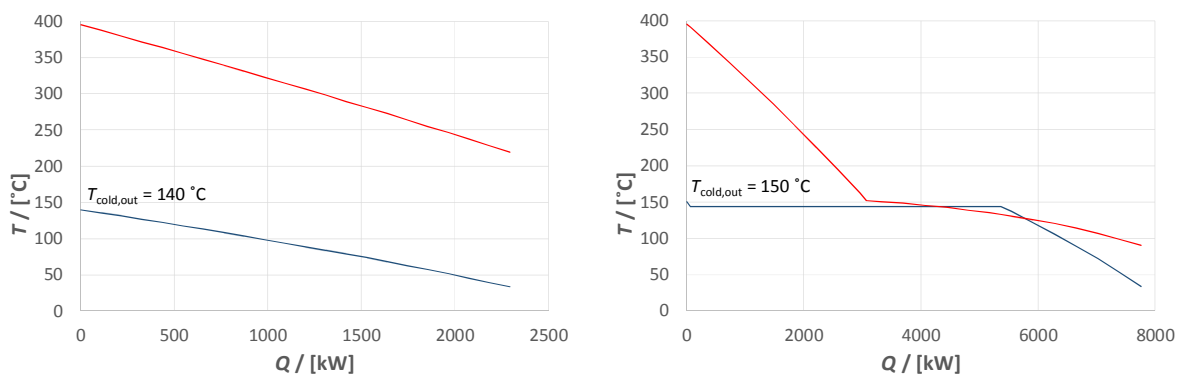


1  
2 **Figure 3.** TAC vs reactor-inlet temperature, for reactors with various lengths. Total annual  
3 cost, pressure drop and reactor-outlet temperature are indicated, for each optimal point.  
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7 **Figure 4.** Methanol conversion versus temperature, at fixed reaction rate.  
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**Figure 5.** T–Q curve of the feed-effluent heat exchanger (FEHE), for two different values of the cold stream outlet temperature.

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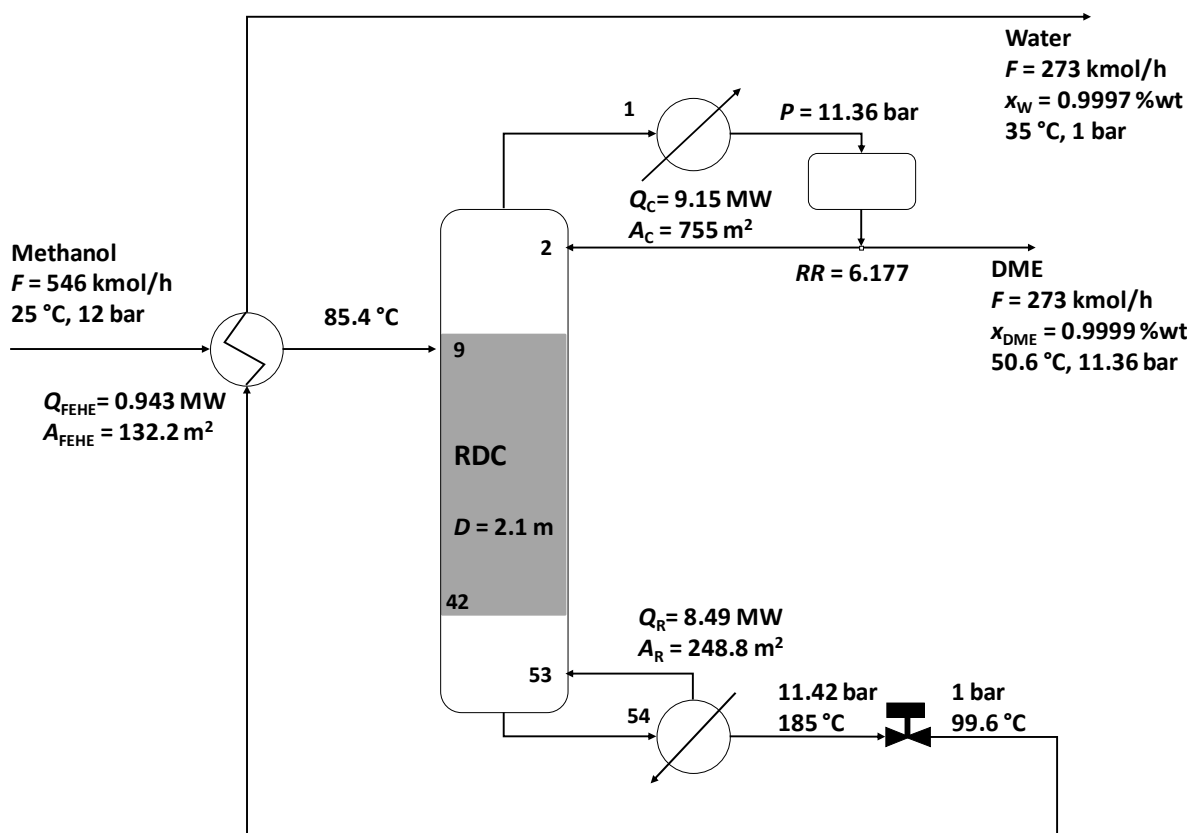
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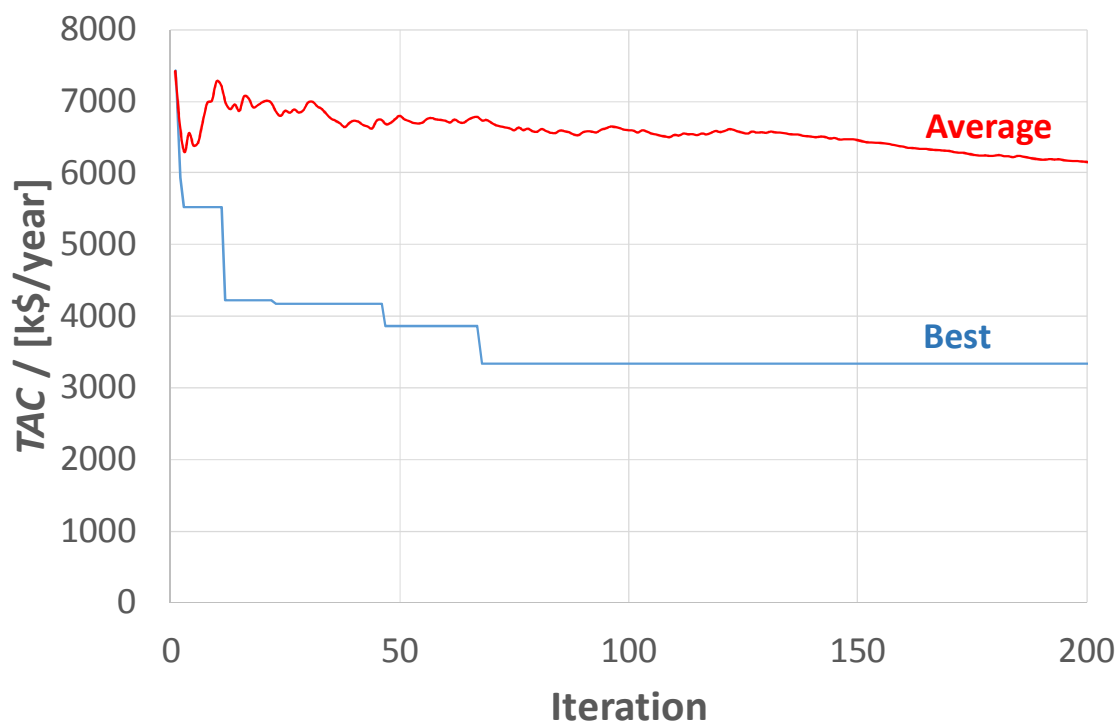
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**Figure 6.** Single step process using a reactive distillation column for DME production

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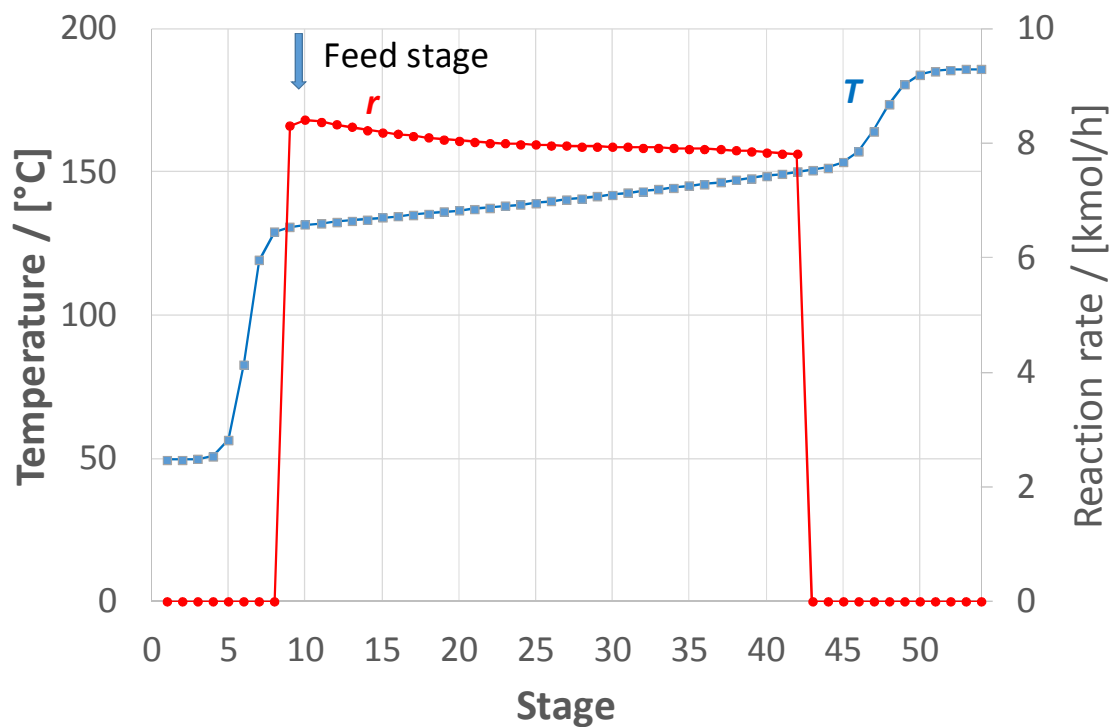
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Figure 7. Progress of the RDC optimization

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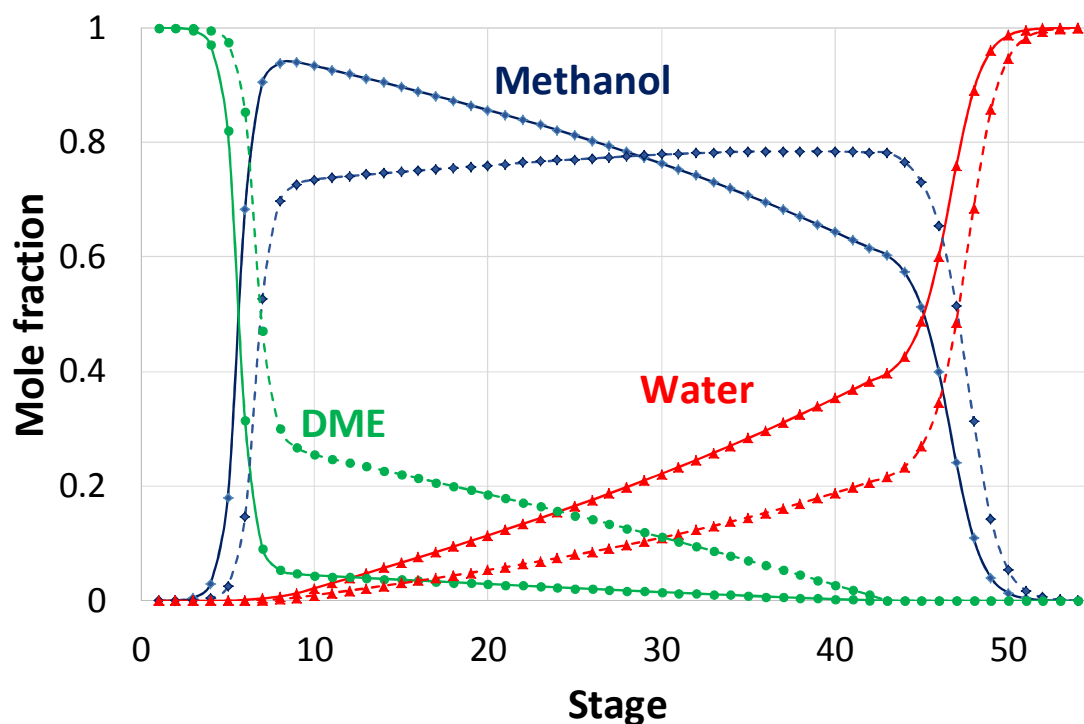


6

Figure 8. Temperature and reaction rate profile along the RD column

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1

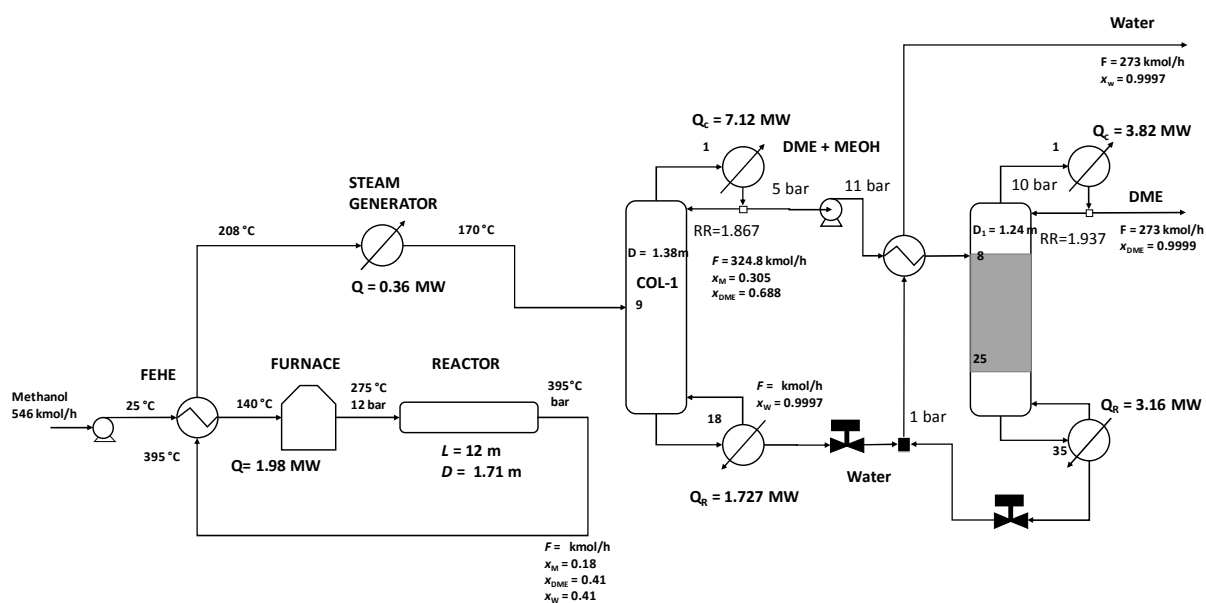


2

3 **Figure 9.** Liquid (continuous line) and vapor (dashed line) composition profiles along the RD  
4 column

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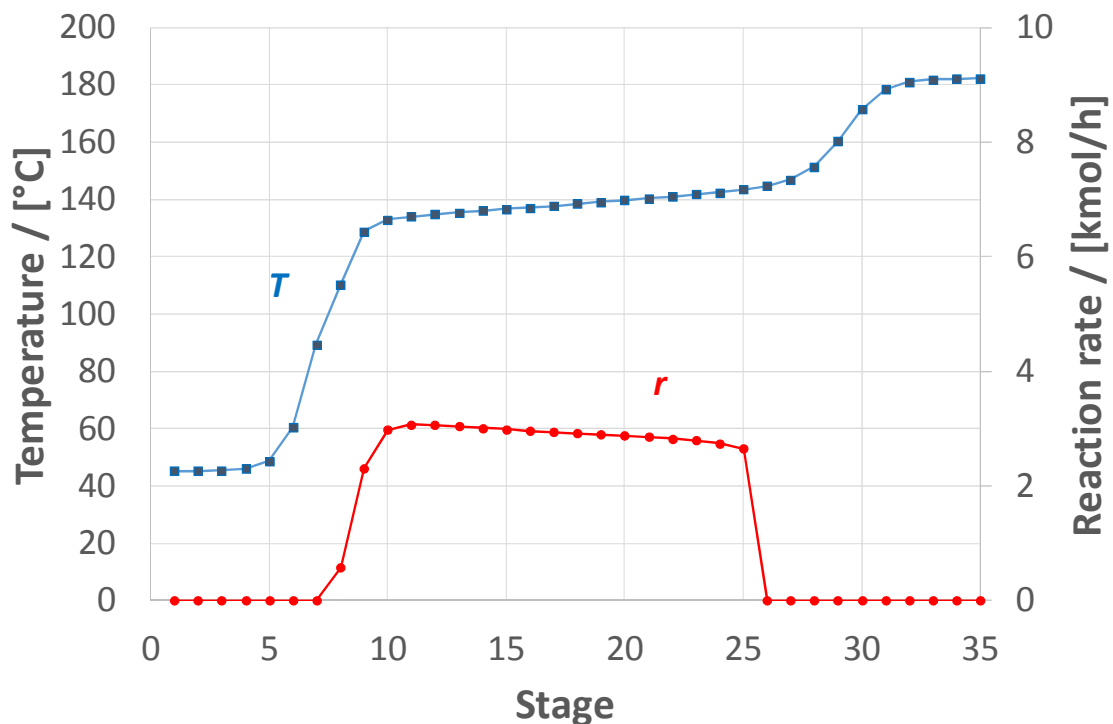


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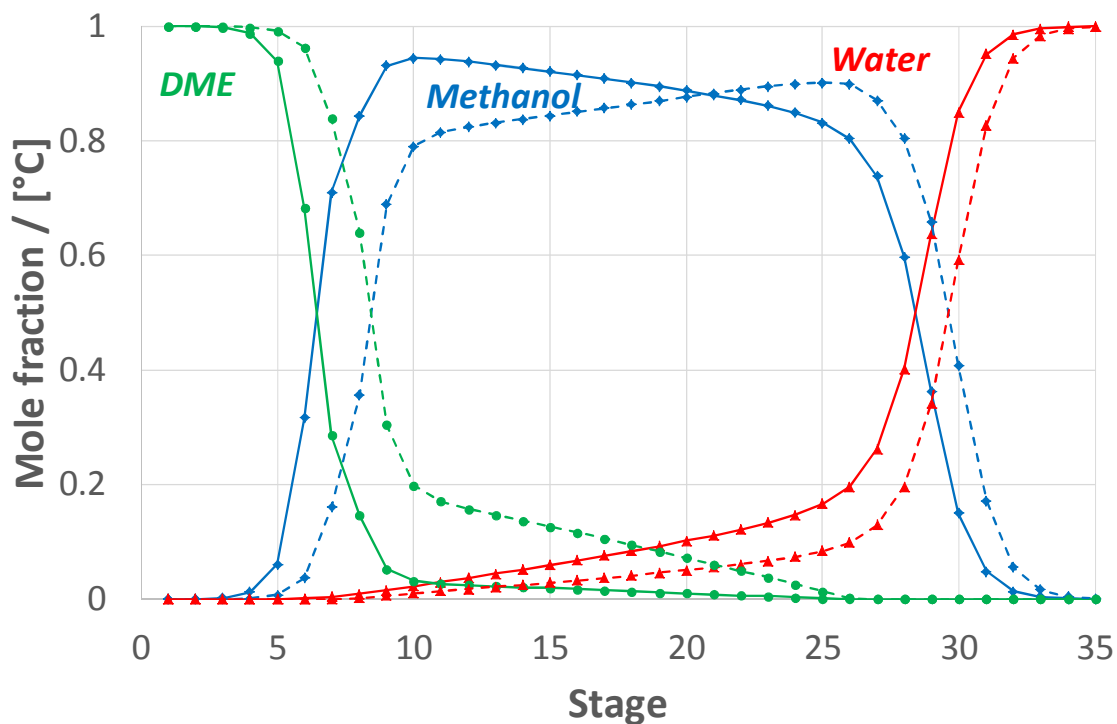
8 **Figure 10.** Combined gas-phase reactor and reactive distillation process for DME production

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 2 **Figure 11.** Temperature and reaction rate profiles along the RD column, in the combined gas-  
 3 phase reactor and RDC process  
 4



5  
 6 **Figure 12.** Liquid (continuous line) and vapor (dashed line) composition profiles along the  
 7 RD column, in the combined gas-phase reactor and RDC process