Electronic Supplementary Material

ESI

Detailed process description

In the following, the processes P0-P4 discussed in the main article are described in detail.

P0: Conventional Process

The conventional process is based on the gas-phase methanol dehydration over γ-Al_2O_3 in an adiabatic fixed-bed reactor as shown in Figure S 1. A detailed description is given by Bildea et al.[7].

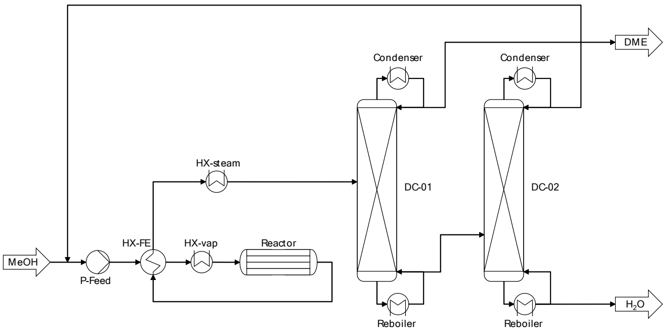

Figure S 1: Process flow diagram of process P0

The crude MeOH is purified in a dedicated CMD column. The pure MeOH is mixed with recycled MeOH from the DME process and then pressurized to the reaction pressure of 12 bar, preheated by the feed-effluent heat exchanger HX-FE and evaporated in HX-vap prior to being fed to the adiabatic reactor, where the gaseous MeOH is dehydrated to DME and H_2O. The reactor effluent is cooled down in HX-FE, the remaining heat is used in the steam generator HX-steam. The cooled, but still gaseous reactor product is then fed to the DME column, where DME is withdrawn as distillate. The bottoms product consisting of MeOH and H_2O is forwarded to the second distillation column where the MeOH distillate is withdrawn and recycled and the water by-product is removed as bottom stream. The stage number and feed stage of both columns are taken from Bildea et al.[7], the column height and diameter were calculated based on the HETP of the packing and the Aspen internal hydraulics tool.

P1: Liquid phase reaction – separation – recycle

A significant energy demand in P0 is required for the evaporation of the MeOH feed. Consequently, in the process P1, the reaction was shifted to the liquid phase to explore the potential of increasing the energy efficiency of the process. Process P1 resembles P0, the major distinction however is the reaction phase being liquid rather than gaseous. This leads to a different reaction temperature and heat integration concept. Instead of an adiabatic reactor, an isothermal reactor is implemented due to the temperature sensitivity of the IER catalysts. The flowsheet of this process is shown in Figure S 2.

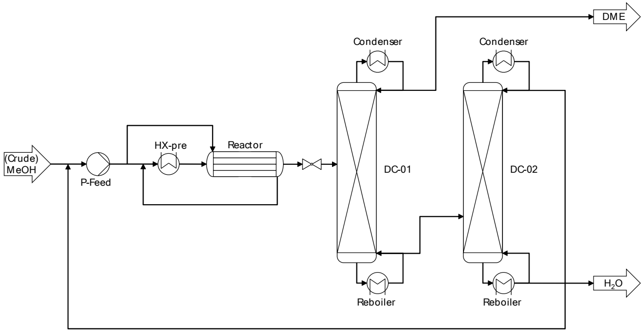

Figure S 2: Process flow diagram of process P1

The cold feed is first mixed with recycled MeOH and then pumped to reaction pressure. The pressurized feed is then partially used as cooling medium for the isothermal liquid phase reactor. Thereby the feed is partially pre-heated. In an additional steam operated heat exchanger HX-pre, the feed is then conditioned to the final reaction temperature. In the liquid phase reactor, the MeOH is partially dehydrated to DME and H_2O. Subsequently the reactor product is throttled and fed to a series of two distillation columns. The pressure level and operating parameters of the distillation columns were adopted from P0.

P2: Stand-alone reactive distillation

P2 is a highly intensified process concept with the RDC being the central unit operation. Figure S 3 shows the corresponding process flow diagram.

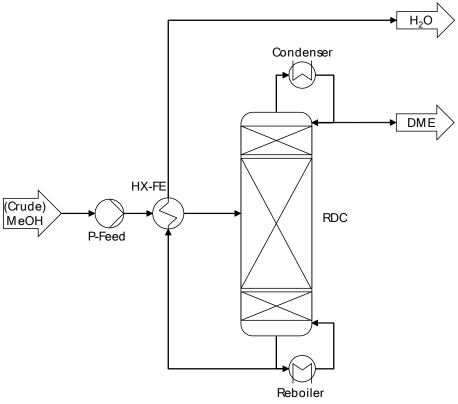

Figure S 3: Process flow diagram of process P2

The feed is first pressurized, and heat integrated with the bottoms product of the RDC by HX-FE before entering the RDC in liquid state on the feed stage N_{Feed}. The size of the reactive section of the RDC is designed to allow a full conversion of the MeOH to DME and H_2O. Two rectifying sections above and below the reactive section are required to purify the products. The bottoms product is pure H_2O and is used to preheat the feed stream. The distillate product is pure DME.

P3: Reactive distillation column with pre-reactor

P3 presents an extension of P2 by adding a PR to the flowsheet. Figure S 4 shows the corresponding flowsheet. This additional reaction volume is expected to allow a smaller RDC which could lead to lower plant cost and energy demand.

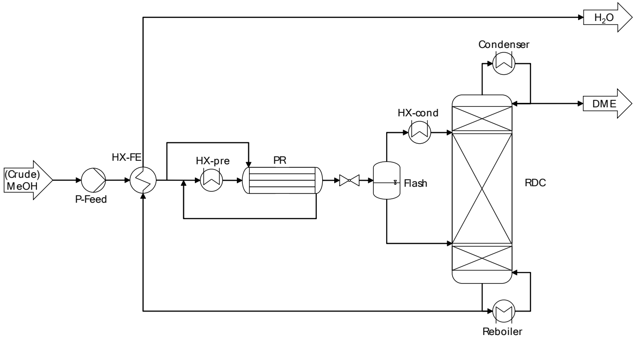

Figure S 4: Process flow diagram of process P3

The fed MeOH is first pumped to the reactor operating pressure, which is significantly higher than the RDC pressure to attain a liquid phase reaction. For A36 and C400, a reactor pressure of 47 bar (T_{max}=130 °C) and 76 bar (T_{max}=160 °C) is required, respectively. The feed is heat integrated with the bottoms product of the RDC via HX-FE and with the PR to allow an isothermal reactor operation and to utilize the exothermic heat for further pre-heating of the feed. The steam operated HX-pre is then used for final feed conditioning. In the PR, MeOH is partially dehydrated, thus reducing the required amount of catalyst in the RDC. Due to the large difference in vapor pressure between DME and H_2O, feeding the reactor effluent to the RDC on a single stage is detrimental for the column profile. Feeding in the upper part of the column would mean introducing significant amounts of water to the reactive section, thus inhibiting the reaction. In contrast, feeding in the lower part of the column would lead to significant amounts of DME in the reactive section, reducing the boiling temperature of the mixture in the reactive section and thus reducing the reaction rate. For this reason, the reactor product is throttled to the column pressure and an adiabatic flash separation is performed between PR and RDC. The DME-rich gas phase is condensed in HX-cond and fed to the upper part of the RDC on stage $N_{Feed,DME\text{-}rich}$ while the H_2O-rich liquid phase is fed to the bottom part of the RDC on stage $N_{Feed,H2O\text{-}rich}$. In the RDC, the residual MeOH from the reactor product is fully converted and DME and H_2O are withdrawn as distillate and bottom stream, respectively.

P4: Reactive distillation column with side-reactor

Process P4 is characterized by a combination of RDC and SR. The underlying process flow diagram is shown in Figure S 5.

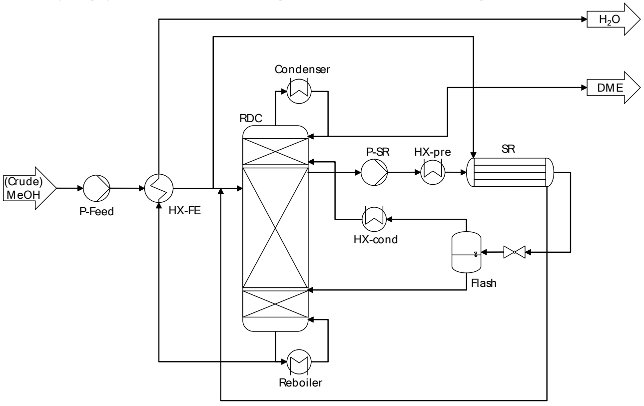

Figure S 5: Process flow diagram of process P4

The feed stream is pumped to the operating pressure and fed to the RDC at N_{Feed}. Heat integration is then performed with the bottom product of the RDC via HX-FE and the preheated feed stream is partially used to cool the SR. The heat integration is analogous to P3. While the unit operations used are the same as in P3, the different arrangement of RDC and reactor gives more degrees of freedom: An additional withdrawal stage N_{WD} is implemented at the RDC, where the feed to the SR is withdrawn with a certain flow rate $\dot{N}_{Side}$, pumped to reaction pressure by P-SR and conditioned by HX-pre to reactor pressure and temperature of the SR. The same reaction conditions apply depending on the catalyst type as already explained for P3. The product mixture is throttled to the operating pressure of the RDC as in P3, and the resulting two-phase mixture is separated in an adiabatic flash separator. The DME-rich phase is condensed in HX-cond and recycled to the top of the RDC at $N_{RCY,\ DME\text{-}rich}$. The water-rich phase is directly recycled to the bottom RDC at $N_{RCY,\ H2O\text{-}rich}$. The RDC itself operates analogous to P2 and P3.

Crude MeOH distillation

In case of a pure MeOH feed to the DME process (case A), the water in the crude MeOH needs to be removed in a dedicated CMD column. Figure S 6 shows the corresponding flowsheet.

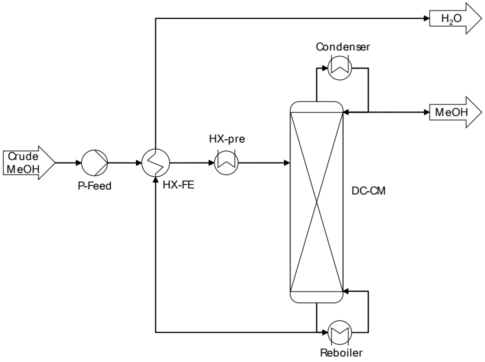

Figure S 6: Process flow diagram of the CMD process.

The crude MeOH is pre-heated in HX-FE, furtherly heated and partly evaporated HX-pre and then fed to the CMD column DC-CM operated at ambient pressure.

Detailed results of crude MeOH distillation step

Table ESI 1: KPI of crude MeOH distillation step

Unit Operation	Parameter	Unit	Value
HX-FE	**Q**	kW	846
HX-pre	**Q**	kW	8606
DC-CM	$\mathbf{H}_{\mathbf{column}}$	m	6
	$\mathbf{d}_{\mathbf{column}}$	m	2
	P	bar	1
	RR	-	1,5
	$\mathbf{Q}_{\mathbf{Reboiler}}$	kW	5500
	$\mathbf{Q}_{\mathbf{Condenser}}$	kW	-13315

Kinetic rate equation for the liquid phase MeOH dehydration

The kinetic rate equation for the liquid phase MeOH dehydration is presented according to Semmel et al.[10] x_i denotes the liquid mole fraction of the component i.

$$r_{DME} = \frac{k \cdot \left(x_{MeOH}^{2} - \frac{x_{DME} \cdot x_{H_2O}}{K_{eq}} \right)}{x_{MeOH}^{2}} \cdot \frac{1}{\left(1 + K_W \cdot x_{H2O}\right)^2} \tag{1}$$

With

$$k = k_0 \cdot \exp\left(\frac{-E_A}{R\,T}\right) \tag{2}$$

$$K_W = \exp\left(K_{W1} - \frac{K_{W2}}{T}\right) \tag{3}$$

$$K_{eq} = \exp\left(1.743 + \frac{887.9}{T}\right) \tag{4}$$

Table ESI 2: Kinetic parameters for the liquid phase MeOH dehydration on the two catalysts A36 and C400 [10].

Parameter	Unit	$A36$	C400
k_0	$mol \cdot kg_{Kat}^{-1} \cdot s^{-1}$	8.089e9	5.973e10
E_A	$kJ \cdot mol^{-1}$	91.56	101.98
K_{W1}	-	−4.2255	0.4118
K_{W2}	K	−2360.9	−345.2587

Kinetic rate equation for the gas phase MeOH dehydration

The kinetic rate equation for the conventional gas-phase DME synthesis from MeOH according to the corrected publication of Bercic et al.[22] X denotes the gaseous mole fraction of the component i in mole percent.

$$r_{DME} = \frac{k_s \cdot K_M^2 \left(X_{MeOH}^{\;2} - \frac{X_{DME} \cdot X_{H_2O}}{K} \right)}{\left(1 + 2 \cdot \sqrt{K_M \cdot X_{MeOH}} + K_W \cdot X_{H_2O} \right)^4} \qquad (5)$$

Table ESI 3: Parameters for the apparent gas phase MeOH dehydration kinetics on industrial sized γ-Al_2O_3 catalyst.[22]

Parameter	Unit	
k_s	$kmol \cdot kg_{Kat}^{-1} \cdot h^{-1}$	$6.6e8 \cdot \exp\left(\frac{-10800}{T}\right)$
K_M	$\%^{-1}$	$7.2e-3 \cdot \exp\left(\frac{830}{T}\right)$
K_W	$\%^{-1}$	$4.5e-3 \cdot \exp\left(\frac{1130}{T}\right)$

Economic and technical assumptions for the TEA

Table ESI 4: Lang factors for the calculation of the fixed capital investment for fluid processing chemical plants based on equipment cost (EC) [28].

Cost component	Basis	Value
Direct plant cost (D)		
Equipment installation	EC	0.47
Instrumentation and control	EC	0.36
Piping (installed)	EC	0.68
Electrical (installed)	EC	0.11
Buildings including services	EC	0.18
Yard improvements	EC	0.1
Service facilities (installed)	EC	0.55
Indirect plant cost (I)		
Engineering and supervision	EC	0.33
Construction expenses	EC	0.41
Legal expenses	EC	0.04
Contingency and contractor's fee		
Contractor's fee	D + I	0.05
Contingency	D + I	0.1

Table ESI 5: Lang factors for the calculation of $OPEX_{ind}$ [28].

Cost component	Basis	Value
Operating Supervision OS	OL	0.15
Maintenance labor (ML)	FCI	0.01
Maintenance material (MM)	FCI	0.01
Operating supplies	ML+MM	0.15
Laboratory charges	OL	0.2
Insurance and taxes	FCI	0.02
Plant overhead costs (PO)	OL+OS+ML	0.6
Administrative costs	PO	0.25

Table ESI 6: Correlation for estimating the operating labour of large scale or fluid processes [28] .

	Sizing parameter	Cost function
Operating labour (OL) in hours/day/processing step	Plant capacity C in kg/day	$OL = 2.05 \cdot C^{0.245}$

Table ESI 7: Heat transition coefficient used for the different heat exchangers in the studied processes.[32]

Heat exchanger	Unit	Heat transition coefficient
Column reboiler	$W\ m^{-2}\ K^{-1}$	1750
Column condenser	$W\ m^{-2}\ K^{-1}$	700
HX-pre	$W\ m^{-2}\ K^{-1}$	1050
HX-cond	$W\ m^{-2}\ K^{-1}$	700
HX-FE (liquid-liquid, P1-P4)	$W\ m^{-2}\ K^{-1}$	700
HX-FE (gas-liquid, P0)	$W\ m^{-2}\ K^{-1}$	200
HX-vap (evaporation)	$W\ m^{-2}\ K^{-1}$	900
HX-vap (superheat)	$W\ m^{-2}\ K^{-1}$	300
HX-steam	$W\ m^{-2}\ K^{-1}$	200

Cost functions for equipment cost

Table ESI 8: Cost functions for calculation of the equipment cost in $\$_{2002}$ and $\$_{2012}$, respectively.

Apparatus	Sizing parameter	Cost function	Source
Pump	$\dot{V}$ in $m^3 \cdot s^{-1}$	$EC_{\$2002} = F_p \cdot (18963.48 \cdot \dot{V}^{0.4} + 222.35)$	Own regression based on Peters et al. [28]
Pump: pressure correction	p in kPa	$F_p = 0.000426 \cdot p + 0.59$	
HEX	A in m^2	$EC_{\$2002} = F_p \cdot (0.00004 \cdot A^3 - 0.08 \cdot A^2 + 93.38 \cdot A \cdot$	Own regression based on Peters et al. [28]
HEX: pressure correction - tube	p in kPa	$F_p = 0.000020 \cdot p + 0.984$	
HEX: pressure correction – tube&shell	p in kPa	$F_p = 0.000070 \cdot p + 0.9349$	
Column shell	h in m, d in m	$EC_{\$2002} = F_p \cdot (4051.28 \cdot d^2 + 3538{,}89 \cdot d + 31.82$	Own regression based on Peters et al. [28]
Column shell: pressure correction	p in kPa	$F_p = 0.00037 \cdot p + 1.2265$	
Reactor (isotherm)	A in m^2	$EC_{\$2002} = F_p \cdot (0.00004 \cdot A^3 - 0.08 \cdot A^2 + 93.38 \cdot A \cdot$	Own regression based on Peters et al. [28]
Reactor: pressure correction	p in kPa	$F_p = 0.000070 \cdot p + 0.9349$	
Reactor: tube diameter	d in m	$F_d = 710.93 \cdot d^2 - 16.56 \cdot d + 0.935$	
Reactor (adiabatic)	d in m, L in m	$EC_{\$2012} = \frac{1536.5}{280} \cdot 957.9 \cdot d^{1.066} \cdot L^{0.82} \cdot (2.18 + F_p$	Bildea et al. [7]
Reactor (adiabatic): pressure correction	p in bar	$F_p = 1 + 0.0074 \cdot (p - 3.48) + 0.00023 \cdot (P - 3.48)$	
Flash[1]	h in m	$EC_{\$2002} = F_p \cdot (-2.29 \cdot h^2 + 387.6 \cdot h + 788.66)$	Own regression based on Peters et al. [28]
Flash: pressure correction	p in kPa	$F_p = 0.00040 \cdot p + 1.2265$	

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[1] Correlation for flash diameter of 0.5 m.

Hydraulic regression function

The hydraulic design of the RDC was conducted according to the methodology presented by Brunazzi et al.[33]. The basis of this design method is a quadratic equation (9) from which the gas velocity can be calculated based on the total pressure drop of the wet packing $\frac{\Delta p_{wet}}{\Delta Z}$. The solution of this equations is thereby limited to positive results.

$$\frac{a \cdot \rho_G \cdot D}{(\sin^2(\theta) \cdot \epsilon^3 \cdot f_s} \cdot u_G^2 + \frac{a \cdot \eta_G \cdot E}{\sin(\theta) \cdot \epsilon^2 \cdot d_{eq}} \cdot u_G - \frac{\Delta p_{wet}}{\Delta Z} \cdot (1 - F \cdot h_{L,Start})^5 = 0 \qquad (9)$$

The quadratic equation is solved at the flooding point to yield the maximum gas velocity $u_{G,max}$ before flooding. At the flooding point, the pressure drop is defined as follows:

$$\left(\frac{\Delta p_{wet}}{\Delta z}\right)_f = \sqrt{\frac{1 - F \cdot h_{L,oc,0}}{11 \cdot F \cdot C \cdot h_{L,oc,0}}} \cdot \rho_L \cdot g \qquad (10)$$

The actual design gas velocity u_G at operating conditions is selected to be 80 % of the maximum gas velocity:

$$u_G = 0.8 \cdot u_{G,max} \qquad (11)$$

The overall calculation method is lengthy, for details the reader is referred to the original literature of Brunazzi et al.[33] and Hoffmann et al.[23].

Table ESI 9 shows the design parameters for the catalytic packing used in this work. They were adopted from the packing MULTIPAK®-II at large column diameters (>1 m) to account for the large production capacity of the plant considered in this work.

Table ESI 9: Used parameters for the catalytic packing.

Parameter	Unit	Value	Source
Specific surface area a	$\frac{m^2}{m^3}$	325	[23]
Void fraction packing ϵ	-	0.35	[23]
Catalyst volume fraction ψ		0.55	[23]
Inclination angel θ	°	45	[23]
Equivalent diameter d_{eq}	m	$\frac{4 \cdot \epsilon}{a}$	[23]
Wall factor f_s	-	1	Approximation for large column diameters
Void fraction catalyst bags ϵ_{CB}	-	0.3	[23]
Catalyst particle diameter d_{cat}	m	0.001	[34]
Packing parameter A	-	0.2	[23]
Packing parameter B	-	0.25	[23]
Packing parameter C	-	150	[23]
Packing parameter D	-	0.024	[23]
Packing parameter E	-	6.6	[23]
Packing parameter F	-	2	[23]

The hydraulic design is carried out for the reactive section only. The reactive stage with the highest gas load is the limiting stage and consequently used as design stage. The resulting column diameter for the reactive section is adopted for the entire column.

For every process and catalyst, varying the catalyst loading per stage different reflux ratios are generated. For each case the diameter of the column is determined according to the procedure just described. From all examined simulations, a regression function was obtained, which was then used to calculate the RDC diameter based on the RR of the respective case in the TEA.

All used hydraulic regression functions are summarized in Table ESI 1.

Table ESI 10: Summary of the hydraulic regression functions for all RDC containing processes P2, P3 and P4 and for both studied catalysts.

Process	Catalyst	Regression function	Validity range
P2	A36	$d_{RDC} =- 1.02E\square\square 8 \cdot RR^6 + 1.07E\square 6 \cdot RR^5 - 4.4$	RR = 8.5-25
	C400	$d_{RDC} =- 1.07E\square\square 9 \cdot RR^6 + 1.64E\square 7 \cdot RR^5 - 1.0$	RR = 2.2-30
P3	A36	$d_{RDC} = 1.74E\square\square 7 \cdot RR^6 - 1.23E\square 5 \cdot RR^5 - 3.45$	RR = 1.7-21
	C400	$d_{RDC} =- 3.1E\square\square 5 \cdot RR^6 + 1.31E\square 3 \cdot RR^5 - 2.23$	RR = 1.6-19
P4	A36	$d_{RDC} =- 6.0E\square\square 9 \cdot RR^6 + 6.0E\square 7 \cdot RR^5 - 3.0E$	RR = 5-25
	C400	$d_{RDC} =- 3.0E\square\square 10 \cdot RR^6 + 8.0E\square 8 \cdot RR^5 - 7.0E$	RR = 1.5-25

For the process P3 with C400 and pure MeOH feed, very low RR are achieved in the optimal configuration. Consequently, very small minimum hydraulic diameters are required which imply a very high column to achieve the desired total volume for the reactive section. To avoid unreasonably slim and high columns, a minimal RDC diameter of 1.5 m was defined for this process.

In all other processes, the RDC diameter according to the hydraulic regression functions were larger than 1.5 anyway.

Key technical parameters of the simulated MeOH plant

The MeOH plant is based on CO_2 and H_2 feedstock and produces enough MeOH required for a DME plant with the production capacity of 100 kt/a. The purge in the MeOH plant was set to a very small purge ratio of 0.01 %.

The key technical parameters of the MeOH process are summarized in Table ESI 11.

Table ESI 11: Key technical parameters of the simulated MeOH process.

Parameter	Unit	Value
N_{Feed, H_2}	$\frac{kmol}{h}$	1638.7
N_{Feed, CO_2}	$\frac{kmol}{h}$	548
SN_{Loop}	$\frac{mol}{mol}$	4.88
$Recycle\ ratio$	$\frac{mol}{mol}$	3.78
$GHSV$	h^{-1}	7569

The stoichiometric number is defined according to Nestler et al.[35] as follows:

$$SN = \frac{y_{H2} - y_{CO2}}{y_{CO2} + y_{CO}} \tag{12}$$

The Recycle Ratio is defined as the ratio between the mole flow of the loop stream and the mole flow of the MUG.

$$Recycle\ Ratio = \frac{N_{Loop}}{N_{MUG}} \tag{13}$$

Whereas the make-up gas (MUG) is the CO_2/H_2 mixture fed to the synthesis loop.

Column profiles of P4

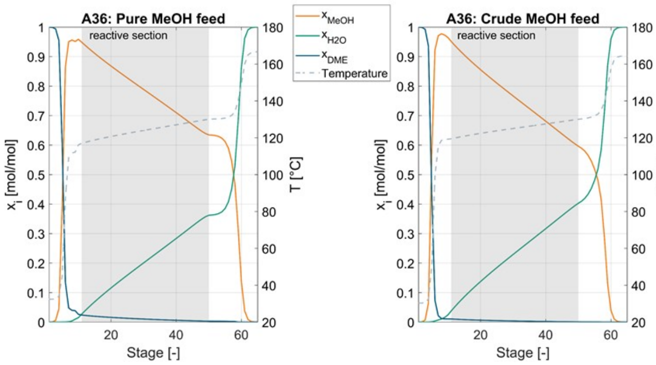

Figure S 7: Liquid composition profile and temperature profile of the RDC in process P4 with A36 as catalyst and pure MeOH feed (left) or crude MeOH feed (right).

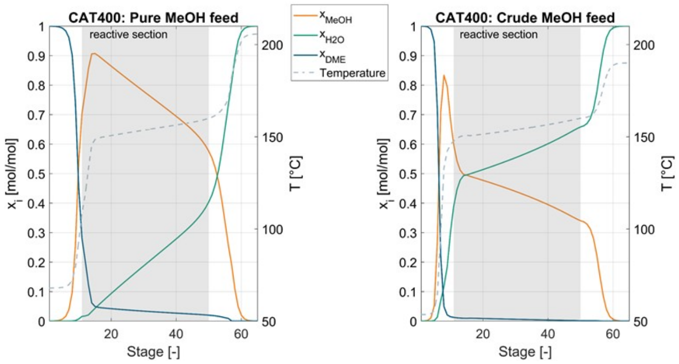

Figure S 8: Liquid composition profile and temperature profile of the RDC in process P4 with C400 as catalyst and pure MeOH feed (left) or crude MeOH feed (right).