

# Novel eco-efficient reactive distillation process for dimethyl carbonate production by indirect alcoholysis of urea

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**Abstract** Dimethyl carbonate is an eco-friendly essential chemical that can be sustainably produced from CO<sub>2</sub>, which is available from carbon capture activities or can even be captured from the air. The rapid increase in dimethyl carbonate demand is driven by the fast growth of polycarbonates, solvent, pharmaceutical, and lithium-ion battery industries. Dimethyl carbonate can be produced from CO<sub>2</sub> through various chemical pathways, but the most convenient route reported is the indirect alcoholysis of urea. Previous research used techniques such as heat integration and reactive distillation to reduce the energy use and costs, but the use of an excess of methanol in the trans-esterification step led to an energy intensive extractive distillation required to break the dimethyl carbonate-methanol azeotrope. This work shows that the production of dimethyl carbonate by indirect alcoholysis of urea can be improved by using an excess of propylene carbonate (instead of an excess of methanol), a neat feat that we showed it requires only 2.64 kW·h·kg<sup>-1</sup> dimethyl carbonate in a reaction-separation-recycle process, and a reactive distillation column that effectively replaces two conventional distillation columns and the reactor for dimethyl carbonate synthesis. Therefore, less equipment is required, the methanol-dimethyl carbonate azeotrope does not need to be recycled, and the overall savings are higher. Moreover, we propose the use of a reactive distillation column in a heat integrated process to obtain high purity dimethyl carbonate (> 99.8 wt-%). The energy requirement is reduced by heat integration to just 1.25 kW·h·kg<sup>-1</sup> dimethyl carbonate, which is about 52% lower than the reaction-separation-recycle process. To benefit from the energy savings, the dynamics and control of the process are provided for ±10% changes in the nominal rate of 32 ktpy dimethyl carbonate, and for uncertainties in reaction kinetics.

**Keywords** dimethyl carbonate, reactive distillation, process design, plantwide control

## 1 Introduction

In view of the climate change and sustainability issues, the process industries have embarked on a quest to develop novel solutions to capture CO<sub>2</sub> and use it as a feedstock in various catalytic processes that can convert it to useful products, e.g., methanol, dimethyl ether, cyclic carbonates and dimethyl carbonate (DMC). DMC is considered an eco-chemical compound because it features low toxicity, fast biodegradability, and can be produced from CO<sub>2</sub> captured from the air [1]. Its molecular structure makes it suitable to replace hazardous chemicals such as dimethyl sulphate, methyl halides, and acylating agents [2]. It is a good competitor among fuel additives and is used also as a solvent to produce polycarbonates or electrolytes for lithium-ion batteries [3].

DMC can be produced through a conventional route (via phosgene, partial carbonylation, or methyl nitrite) or CO<sub>2</sub> based route such as direct synthesis from CO<sub>2</sub> and methanol, urea route, ethylene carbonate (EC) route, or propylene carbonate (PC) route [4]. Table 1 lists these processes and also the energy requirements to obtain DMC as high purity product. The energy required to produce urea which is 12.73 MJ·kg<sup>-1</sup> DMC [4] is included for all the urea routes listed in Table 1. Some of these routes (e.g., direct synthesis from CO<sub>2</sub> and methanol) are clearly more energetically unfavourable than the others. The phosgene route is the traditional method to produce DMC, but it uses an extremely toxic material [5,9]. The Bayer process is used for low production rate, and encounters difficulties in the downstream process due to the presence of a binary azeotrope in the methanol-water-DMC mixture [4]. The DMC processing route from methyl nitrite uses nitric oxide, which is toxic and with safety issues [5]. The direct

**Table 1** DMC production processes and the energy usage

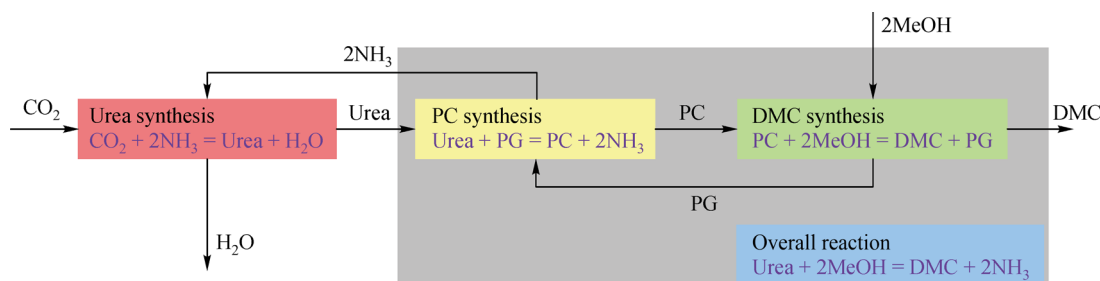
Process for DMC production	Energy intensity/(MJ·kg <sup>-1</sup> ) DMC	Ref.
Phosgene	n/a	[5]
Bayer	10.55	[4]
Methyl nitrite	n/a	[5]
CO <sub>2</sub> direct synthesis	48.99	[6]
Urea route	72.09	[4]
EC	29.36	[4]
PC (excess of methanol)	28.57	[7]
PC (excess of PC)	22.23	[8]

synthesis of DMC from CO<sub>2</sub> and methanol requires critical operating conditions (temperature and pressure) and a huge amount of energy for CO<sub>2</sub> activation, giving a low DMC yield even when reactive separations are used [9–11].

The urea route involves two reaction steps: 1) synthesis of urea from NH<sub>3</sub> and CO<sub>2</sub>; 2) production of DMC from urea and methanol, while methylcarbamate is formed as intermediate component. The operating conditions are milder than the previously reported processes, yet the purification of DMC by pressure swing distillation is a very energy-intensive process [4]. For the EC route, ethylene oxide (which is a toxic compound) is required as raw material and the EC reactor requires extreme reaction conditions (588 °C, 125 bar) to produce it, though the process is more efficient [4]. Lately, a new improved pathway has been discovered to produce DMC by indirect alcoholysis of urea (PC route). The production of DMC by indirect alcoholysis of urea is an environmentally friendly method, due to the use of CO<sub>2</sub> captured from the air, the use of two reactants that are regenerated in the process (propylene glycol (PG) and NH<sub>3</sub>), and rather mild operating conditions. The process requires three reaction steps: 1) urea synthesis from NH<sub>3</sub> and CO<sub>2</sub>; 2) PC synthesis from urea and PG; 3) DMC synthesis from PC and methanol (as illustrated in Fig. 1). In the reaction between urea and PG, one of the products (NH<sub>3</sub>) has a low boiling point and can be easily removed from the reaction mixture. Therefore, the chemical equilibrium does not impose any serious constraint and high conversions can be

achieved. However, the DMC synthesis is a reversible reaction which can be performed using an excess of methanol or an excess of PC to enhance the conversion. High conversion of PC can be obtained when a reactive distillation column (RDC) is used [3]. However, the drawback of using an excess of methanol is that only a DMC-methanol mixture with azeotropic composition can be obtained from RDC, and new energy-intensive separation steps are required to obtain high DMC purity by extractive distillation or pressure swing distillation [7,8,12]. More recently, a novel reaction-separation-recycle (RSR) process using conventional technology was developed, where the DMC synthesis takes place at an excess of PC, allowing to obtain high purity DMC, while recycling the DMC-methanol azeotrope [8]. However, that process using conventional operating units could be significantly improved further by employing RD as an effective process intensification technology. Shi et al. [7] developed such a process where reactive distillation technology and heat integration are used to reduce the total annual cost (*TAC*). Indeed, reactive distillation technology and heat integration can offer significant advantages, but the drawback of that process is the use of an excess of methanol for the DMC synthesis, which leads to an azeotropic composition of DMC-methanol product. Further, the separation of this mixture by extractive distillation or pressure swing distillation is an energy-intensive process and makes the use of an excess of methanol unfavourable [12,13].

To address this issue, the production of DMC by indirect alcoholysis of urea was recently improved by using an excess of PC instead of methanol in a reaction-separation-system. This approach has led to 35% energy savings [8], as compared to the sequence where DMC was produced with an excess of methanol [8]. However, no process intensification methods were employed, despite the appeal of using a RDC for DMC synthesis, which can bring many advantages such as reduction of the equipment required, elimination of DMC-methanol azeotrope recycle, reduction of the energy requirements and the *TAC*. To solve these issues, this work proposes an enhanced process for DMC synthesis in a RDC, where an excess of PC is used. All distillation columns (DCs) are optimized, the overall


**Fig. 1** DMC synthesis by indirect alcoholysis of urea (PC route).

energy requirement is reduced by energy integration, and the sustainability of the process is improved by several key metrics. A control structure is also proposed to ensure a good control of the new DMC process. Aspen Plus and Aspen Plus dynamics are used for process design, process control, and evaluation.

Overall, this original research paper, invited for the special issue on multiscale process and energy systems engineering, is the first to propose a new reactive distillation process for DMC synthesis using an excess of PC (instead of methanol as reported in all previous articles about DMC synthesis by reactive distillation) and avoiding the DMC-methanol azeotrope separation. In this respect, it covers several PSE topics of interest for this special issue, such as process design for sustainable chemicals production, CO<sub>2</sub> utilization, as well as process dynamics and control.

## 2 Experimental

This section presents the basic data and methods required for the complete process design and simulation of the new DMC process, in terms of thermodynamic data, chemistry and kinetics.

### 2.1 Thermodynamic data

The physical properties of all pure components involved in the DMC process are available in Aspen Plus v10.0 database. The binary interaction parameters of the NRTL model have been properly regressed using experimental data retrieved from the NIST database. For the MeOH-DMC mixture, the experimental data from literature was used [14,15]. For the DMC-PC and DMC-PG mixture, the data from Luo et al. [16] was used, while Mathuni et al. [17] provided the data for the regression of the PC-PG binary parameters. Table 2 presents the boiling points of the pure components and azeotropes, along with the destination of the chemical species after the separation steps are performed. Table 3 lists all the binary interaction parameters used in the Aspen Plus simulations.

### 2.2 Chemistry and kinetics

The main chemical reactions taking place in the urea-based DMC process are equilibrium limited, as presented in Eqs. (1), (2) and (4). The urea reactant required for the production of PC can be synthesized from NH<sub>3</sub> and CO<sub>2</sub>, see Eq. (1). Kongpanna et al. [4] provided a process where a ratio of 4.25:1 for NH<sub>3</sub>:CO<sub>2</sub> is used to obtain 73.8% urea

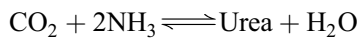
**Table 2** Boiling points of pure components and azeotropes (1 bar)

Component	Boiling point ( $1.013 \times 10^5$ Pa)/°C	Destination
NH <sub>3</sub>	−33.34	Recycle to urea synthesis process
DMC/MeOH azeotrope (0.14/0.86 mol fraction)	63.61	Methanol consumed in RDC
MeOH	64.5	Consumed in RDC
DMC	90.2	Product
Urea	133	Almost complete conversion, small amounts pass through the DMC synthesis process and are recycled
PG	187.7	Recycle from DMC synthesis to PC synthesis
PC	241.8	Recycle, within the DMC synthesis process

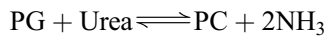
**Table 3** Binary interaction parameters

Component <i>i</i>	Component <i>j</i>	$A_{ij}$	$A_{ji}$	$B_{ij}/^{\circ}\text{C}$	$B_{ji}/^{\circ}\text{C}$
MeOH	DMC	10.3134	−1.59695	−2999.76	547.54
MeOH	PG	0	0	1088.26	−478.899
PC	DMC	−13.0479	−18.6292	8171.48	7346.46
PG	DMC	0.785035	0.81429	50.1177	−4.81697
MeOH	PC	0	0	191.527	92.4028
PC	PG	0.547578	0.948968	0.688674	0.490589
NH <sub>3</sub>	DMC	0	0	−1086.99	2923.74
NH <sub>3</sub>	MeOH	42.312	7.06459	−12020.9	−2887.41
NH <sub>3</sub>	PC	0	0	−1129.71	3183.35
NH <sub>3</sub>	PG	1.17657	−2.1687	0	0

yield by operating the reactor at 180 bar and 160 °C. As this step has been fully reported [4], it is not included here. The energy requirement for urea production is 12.73 MJ·kg<sup>-1</sup> DMC and is included in Table 1 for all urea routes. PC can be produced in the liquid phase reaction of urea and PG as shown in Eq. (2)—by using MgO as solid catalyst. PG is generated and recycled from the transesterification reaction of PC with methanol as shown by Eq. (4). NH<sub>3</sub> can be recycled to the urea synthesis process. For a catalyst concentration of 2 wt-%, Shi et al. [7] provided the reaction rate described by Eq. (3). Equation (3) gives a good approximation for the rate of reversible reaction (2) because one of the reaction products (NH<sub>3</sub>) has low concentration, being removed by vapor-liquid separation.



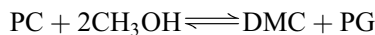
$$\Delta H_{\text{Reaction-1}} = -2312 \text{ kJ} \cdot \text{kmol}^{-1}, \quad (1)$$



$$\Delta H_{\text{Reaction-2}} = 34386.5 \text{ kJ} \cdot \text{kmol}^{-1}, \quad (2)$$

$$\begin{aligned} r_1 &= k \cdot C_{\text{PG}} \cdot C_{\text{Urea}}, \text{ with } k(T) (\text{m}^3 \cdot \text{kmol}^{-1} \cdot \text{s}^{-1}) \\ &= 0.02646 \cdot \exp\left(-\frac{562.6}{T}\right). \end{aligned} \quad (3)$$

DMC is produced in the transesterification reaction of PC with methanol as shown in Eq. (4). This reaction is catalyzed by strongly basic quaternary ammonium ion exchange resins with hydroxide counter ions. The most active solid catalyst which can be used for this reaction is Amberlyst A-26(OH) [18]. The power-law reversible kinetics is given in Eq. (5).



$$\Delta H_{\text{Reaction-3}} = 24432.3 \text{ kJ} \cdot \text{kmol}^{-1}, \quad (4)$$

$$r = k x_{\text{PC}} x_{\text{MeOH}}^2 \left( 1 - \frac{1}{K_x} \frac{x_{\text{DMC}} x_{\text{PG}}}{x_{\text{PC}} x_{\text{MeOH}}^2} \right). \quad (5)$$

The experimental data provided by Pyrlik et al. [18] has been regressed and the following kinetic parameters were determined [8]:  $k_{(313 \text{ K})} = 0.4166 \times 10^{-3} \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$  and  $K_{x(313 \text{ K})} = 0.2$ .

As it will be shown later the temperature in the RDC is not constant, reaching values as high as 373 K on some trays. Thus, the use of temperature-independent reaction rate and equilibrium constants deserves a special discussion. Because the reaction rate constant increases with temperature, the reaction rate is actually faster than predicted by the kinetics. Thus, the use of the constant

value  $k_{(313 \text{ K})}$  leads to a conservative design. The equilibrium constant also changes with temperature. The reaction enthalpy calculated by Aspen Plus by using appropriate models (for which all the parameters are available in the pure-components database) is positive, and one can predict that the equilibrium constant also increases with temperature (endothermal reaction). In this case, the chemical equilibrium is actually more favourable, and the use of the constant value  $K_{x(313 \text{ K})}$  is also conservative. However, experimental results indicate a slightly exothermal reaction with an enthalpy of  $-9522 \text{ kJ} \cdot \text{kmol}^{-1}$  [19]. In this case, the application of van't Hoff equation leads to  $K_{x(313 \text{ K})}/K_{x(373 \text{ K})} = 1.8$ , and the use of  $K_{x(313 \text{ K})}$  results in an optimistic design. The resiliency of the process designed based on temperature-independent kinetics to the uncertainty of the reaction kinetics is checked in the section dedicated to process dynamics and control.

The stoichiometric value for MeOH/PC reaction is 2:1. Higher values of the PC conversion are possible when the methanol is in excess, but when the MeOH/PC feed ratio exceeds 3.4, the composition of the reactor-outlet mixture is such that, if only conventional distillation is used, it can be separated in high purity MeOH and DMC/MeOH azeotrope [8]. Thus, in order to obtain high purity DMC, the MeOH:PC feed ratio must be set at a low value—lower values making easier to obtain high purity DMC (and DMC/MeOH azeotrope), but at the cost of larger PC recycle. In a preliminary design, the MeOH/PC feed ratio was initially set to 2:4 = 0.5. However, the optimization procedure indicated that the optimal ratio is 2:3.26 = 0.613, a value which makes MeOH to be the limiting reactant. Note that the feed ratio is not a decision variable in the optimization, being actually a resulting value due to the way the simulation is set up, since it depends (among others) on the amount of catalyst in the RDC. In a RDC, the conversion of methanol can be influenced by the amount of catalyst, the amount of co-reactant (PC), or the number of reactive stages. The amount of catalyst which can be retained in the packed tray is limited and a large number of reactive stages lead to high investment costs. However, an excess of PC can lead to high conversion of methanol. The PC in excess is recycled in the process, while the PG (by-product of the DMC synthesis) is recycled to PC synthesis process.

### 3 Results and discussion

This section presents the novel reactive distillation process for the DMC production process by indirect alcoholysis of urea (with an excess of PC), considering an annual production of 32 ktpy DMC (99.8 wt-%). Optimization is used to reduce the *TAC*, while heat integration is used to reduce the energy requirements. The process design and rigorous simulations carried out in Aspen Plus are presented in detail along with an economic evaluation of

the process. The sustainability of this process design is proven by several industrial key metrics. Moreover, an effective plantwide control structure is developed, which responds well to disturbances, such as  $\pm 10\%$  changes in the DMC production.

### 3.1 Process description

DMC production by indirect alcoholysis of urea requires three reaction steps (see Fig. 1): 1) urea synthesis from  $\text{NH}_3$  and  $\text{CO}_2$ ; 2) PC synthesis from urea and PG; 3) DMC synthesis from PC and methanol.  $\text{NH}_3$  is the by-product of PC synthesis, and the PG is the by-product of the DMC synthesis, both being recycled in the overall process.

The flowsheet presented in Fig. 2 consists of two processes, corresponding to PC synthesis and DMC synthesis shown in Fig. 1. The PC formation (from PG and urea) occurs in continuous stirred tank reactors (CSTR1 and CSTR2), while the DMC formation (from PC and methanol) occurs in RDC. The PC production process extends from the reactor CSTR1 to the distillation column C1. The reaction between urea and PG (fed at stoichiometric ratio) takes place at  $180^\circ\text{C}$  and 10 bar, in a series of two liquid-phase stirred reactors, in the presence of  $\text{MgO}$  solid catalyst (2 wt-% concentration). These reaction conditions correspond to the experimental conditions under which the kinetics was determined [7]. Part of the  $\text{NH}_3$  formed in the first reactor is removed in a vapour-liquid separator. This allows almost complete urea conversion in the second reactor (CSTR2), where more

$\text{NH}_3$  is produced. Distillation column C1 separates the PC (sent to the DMC production process) from the un-reacted  $\text{NH}_3$ .

The DMC production process includes the RDC and the distillation column C2. The main unit is the RDC. Here, the reaction between PC and methanol takes place. Liquid PC (the heavy reactant) is fed at the top of the column, while methanol is fed to the lower section of the column. The stoichiometric value of the methanol/PC ratio is 2 but in order to obtain high purity DMC, this ratio is kept below 2, at 0.613. Figure 3 shows the temperature and composition profiles of the RDC and DCs.

Due to large excess of PC, the methanol conversion is high, and the distillate product is high purity DMC. Thus, combining reaction and separation is effective in breaking the MeOH/DMC azeotrope. Heavy species—the PG product and the excess PC are removed with the bottom stream. This stream is sent to the vacuum-operated column C2, which separates PG as distillate (recycled to the PC synthesis process) and PC (recycled to the RDC). Note that PC is recycled within the two combined processes, therefore only a small makeup is needed to compensate the losses. The mass balance of the main streams and the characteristics of the equipment are shown in Fig. 2.

### 3.2 Process design

#### 3.2.1 Propylene carbonate synthesis part

Two CSTRs were necessary for 99.3% conversion of PG.

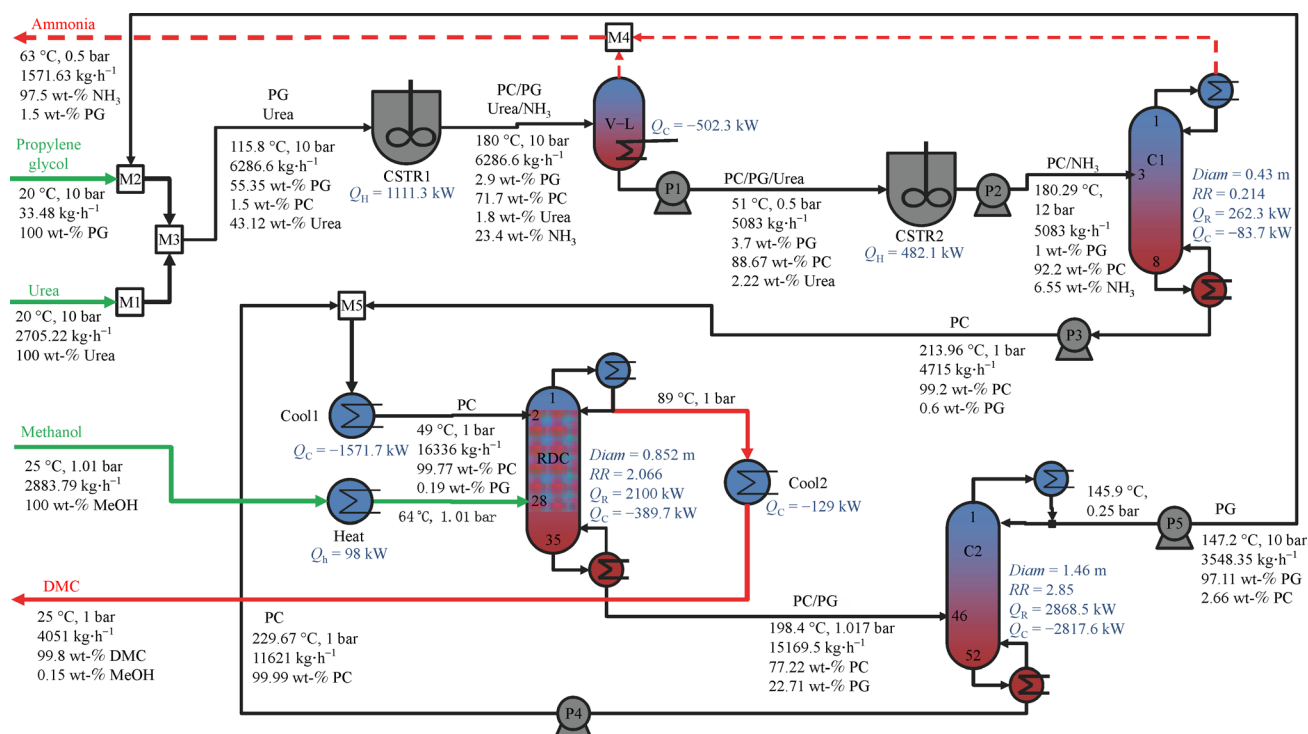
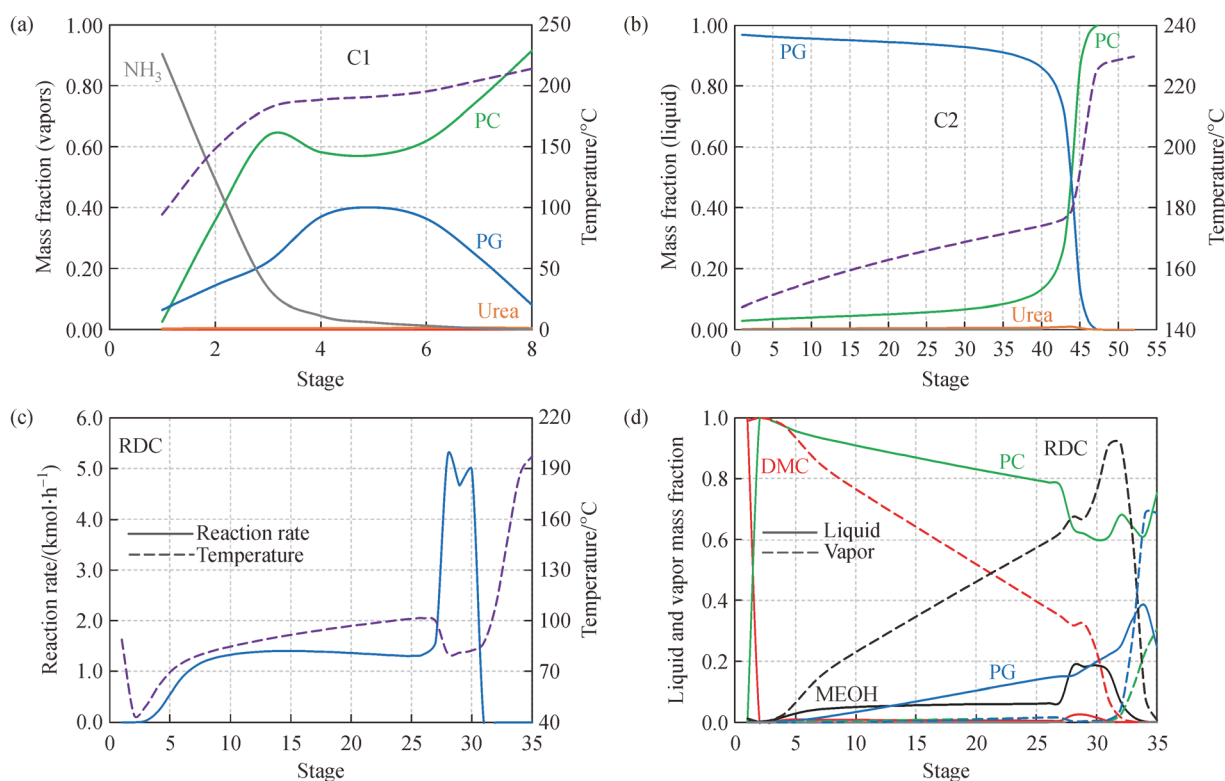


Fig. 2 Flowsheet of the DMC process (DC&RDC).



**Fig. 3** (a) and (b) Temperature and composition profiles of the DC C1; (c) temperature and reaction rate profiles and (d) liquid-vapour composition profiles along the RDC.

For the same reaction volume, a series of CSTRs offers a higher conversion compared to a single one. The volume of the reactors is sufficiently large to allow almost complete conversion of urea. Each reactor has a volume of 20 m<sup>3</sup>, contains 2 wt-% MgO catalyst and operates at 180 °C and 10 bar. The solid catalyst can be retained inside the reactor by placing it in baskets, or alternatively it can be separated in a cyclone or an external decanting unit and recycled. The NH<sub>3</sub> produced in the reactor CSTR1 is removed from the process through a vapour-liquid (flash) unit which operates at 0.5 bar and 50 °C. The NH<sub>3</sub> produced in the second reactor CSTR2 is removed from the top of the C1 distillation column. This column is optimized (see process optimization section) with eight theoretical stages (sieve type) with the feed on stage 3. The operating pressure is 0.5 bar, with a pressure drop of 0.01 bar on each stage (due to the high temperature in the bottom). The condenser is designed as partial-vapour and the reboiler is kettle type.

### 3.2.2 DMC synthesis part

The RDC is designed and optimized to minimize the *TAC*. The optimum number of theoretical stages required is 35, with the PC feed on stage 2, and the methanol feed on stage 28. The reactive stages, the feed stages, and the temperature of the feed streams were found by performing

sensitivity analysis (included in Aspen Plus software) and the ones leading to minimum of reboiler duty were chosen. This is actually the best solution that was obtained by sensitivity analysis, without claiming that it is the global optimum. The condenser is designed as total condenser and the reboiler as a kettle reboiler. The internals of the column are designed as packed stages (type MellapakPlus 252Y or Katapak-SP for the reactive stages) with a height equivalent to a theoretical plate (*HETP*) of 0.4 m. The reactive column operates at 1 bar, with a pressure drop of 0.5 mbar per stage. The amount of the catalyst is found by using Eq. (6):

$$m_{\text{cat,max}} = HETP \frac{\pi}{4} D_{\text{packing}}^2 \phi_{\text{cat}} \rho_{\text{cat,bulk}}, \quad (6)$$

where *HETP* = 0.4 m, column diameter (*D*) = 0.84 m, volume (%) of the catalyst  $\phi_{\text{cat}} = 0.4$ , catalyst density  $\rho_{\text{cat,bulk}} = 675 \text{ kg} \cdot \text{m}^{-3}$  Amberlyst A-26(OH), which results in a catalyst amount of 60 kg·stage<sup>-1</sup>.

The distillation column C2 is designed and optimized for a minimum of the *TAC*. This column has fifty two stages (sieve trays) and the feed stage (46) is chosen for a minimum reboiler duty. The column operates at 0.25 bar, with a pressure drop of 10 mbar. A kettle reboiler and a total condenser are considered for this column. Note that a low operating pressure was selected in order to keep a lower temperature in the column and allow the use of HP

steam in the reboiler while also avoiding thermal degradation.

### 3.3 Process optimization

The purpose of optimization is the minimization of the *TAC* of DCs. The volumes of the two CSTR reactors were fixed, in order to achieve almost complete urea conversion. A payback of 3 years and 8000 h per year of operation was assumed. The capital cost was evaluated according to Dimian [20].

$$TAC = OPEX + \frac{CAPEX}{\text{payback period}} \quad (7)$$

Initially, all the DCs were designed to meet the product quality. Then, for the optimization of each column (Fig. 4), the following design specifications were introduced in Aspen Plus: 1) For the distillation column C1, 99.8% PC recovery in the bottom by varying the reflux ratio;  $10^{-6}$  mol-%  $\text{NH}_3$  in the bottom by varying the molar flow rate of bottom product. 2) For the distillation column C2, 98 mol-% PG purity in distillate by varying the reflux ratio; 98.6 wt-% urea recovery in distillate (to avoid urea accumulation in PC recycling) by varying the molar flow rate of distillate. 3) For the RDC, 99.8 wt-% DMC purity in distillate by varying the reflux ratio;  $1.6 \text{ kg} \cdot \text{h}^{-1}$  mass flow rate of MeOH in the bottom by varying the mass flow rate of distillate. The next step was to perform sensitivity analysis to find, for a given number of stages (*NT*), the feed

stage leading to the minimum reboiler duty, and then to evaluate the *TAC*. The procedure was repeated with a different *NT* value, until the minimum *TAC* was found. For optimal design of the DCs, the ratio between reactants fed to RDC was MeOH:PC = 0.613.

The heating and cooling costs taken into account are [21,22]: high pressure steam (41 bar, 254 °C, 9.88 US\$ ·  $\text{GJ}^{-1}$ ), and cooling water (1 bar, 25 °C, 0.72 US\$ ·  $\text{GJ}^{-1}$ ). The capital expenditures (*CAPEX*) include the heat exchangers, DCs, packing trays, reactors, vapor-liquid vessels, and coolers. The cost of the equipment was estimated by using standard cost correlations [20]:

$$C_{\text{HEX}}(\text{US\$}) = (M\&S/280) \times (474.7A^{0.65}) \times [2.29 + F_m(F_d + F_p)], \quad (8)$$

where *M&S* is the Marshall & Swift equipment cost index (*M&S* = 1638.2 at the end of 2018), *A* is the area ( $\text{m}^2$ ),  $F_m$  = 1 (carbon steel),  $F_d$  = 0.8 (fixed-tube),  $F_p$  = 0 (less than 20 bar). A heat transfer coefficient  $U = 850 \text{ kcal} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{K}^{-1}$  was assumed to calculate the heat transfer area. For the reboilers, the design factor was taken as  $F_d = 1.35$ .

The diameter of the DCs (*D*) was obtained by the tray sizing utility from Aspen Plus, while the height was evaluated as  $H = 0.6 \times (NT - 1) + 2$  (m). The cost of the columns shell was calculated as:

$$C_{\text{shell}}(\text{US\$}) = (M\&S/280) \times (957.9 \times D^{1.066} \times H^{0.82})$$

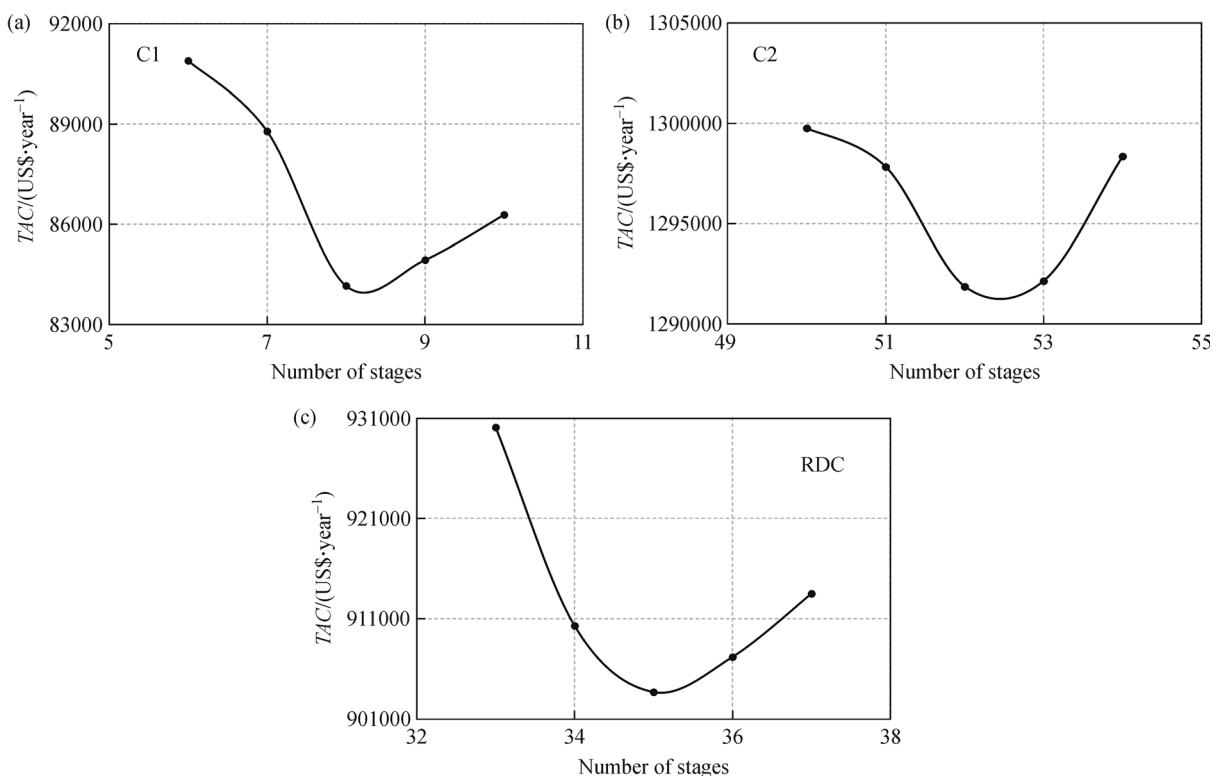


Fig. 4 Optimization of the DCs (a) C1, (b) C2 and (c) RDC for the DMC process.



$$\times (2.18 + F_c), \quad (9)$$

where  $F_c = F_m \cdot F_p$ ,  $F_m = 1$  (carbon steel) and  $F_p = 1 + 0.0074 \cdot (P - 3.48) + 0.00023 \cdot (P - 3.48)^2$ , with pressure  $P$  expressed in bar. The cost of the trays was given by:

$$C_{\text{trays}}(\text{US\$}) = NT(M\&S/280) \times 97.2 \times D^{1.55} \times (F_t + F_m), \quad (10)$$

with  $F_t = 0$  (sieve trays) and  $F_m = 1$  (carbon steel). The cost of the packing was given by:

$$C_{\text{packing}}(\text{US\$}) = \pi D^2 / 4 \times HETP \times (NT - 1) \times \text{packing cost}, \quad (11)$$

with a packing cost of 10000 US\$.m<sup>-3</sup>. According to literature [22], the most expensive random packing stainless steel type is about 3200 €.m<sup>-3</sup>, and the structured packing for RDC is more expensive. Thus, we assume that the structured packing is three times the cost of random packing, which is approximately 10000 US\$.m<sup>-3</sup>.

### 3.4 Energy integration

The heating and cooling targets are identified by pinch analysis, employing the energy analyzer tool from Aspen Plus. The composite curve from Fig. 5 (left) predicts that 2.04 MW (heating and cooling) could be saved by process to process heat transfer. The vapour from the top of column C2 has high temperature and require a high amount of energy for cooling, which can be used as a heating duty. Looking at the temperature profile of the RDC it can be seen that the temperature drops from 199 °C to 80 °C, from reboiler to stage 30. Adding a side reboiler for stage 30 (Fig. 6), the composite curve (Fig. 5 right) shows a potential of 2.73 MW (heating and cooling) which could be reduced by heat integration.

In the heat integrated process shown in Fig. 7, the heating duty is reduced by 1.84 MW (by 25.45%, from

7.23 to 5.39 MW) and the cooling duty is reduced by 1.74 MW (by 32.46% from 5.36 to 3.62 MW). Though the potential of energy savings by heat integration was 2.73 MW (which represents 37.86% of 7.23 MW), less is achieved due to the requirements of many small heat exchangers (HEX), in which case the associated capital cost exceeds the energy savings, so a trade-off is required between CAPEX and operating expenditures (OPEX). The temperature profiles of the cold and hot streams from HEX1, HEX2, HEX3 and HEX4 are presented in Fig. 8. A minimum logarithmic mean temperature difference of 10 K is ensured in all heat exchangers. The complete heat exchanges network is presented in Fig. 9. Compared to the similar process developed in our previous work [8], this process achieves 52% energy savings (34.6% comes from using a RDC and other 17.4% from heat integration). Table 4 provides in detail the energy requirements for two processes: one which uses a reactor and conventional DCs (Conv. DC), another with a DC&RDC, and both heat-integrated (Conv. HI-DC and HI-DC&RDC). Compared to the first conventional heat integrated process (Conv. HI-DC) the energy requirement for heating was reduced from 2.64 kW.h.kg<sup>-1</sup> DMC to 1.25 kW.h.kg<sup>-1</sup> DMC in the heat integrated process shown in Fig. 7 (HI-DC&RDC).

### 3.5 Economic evaluation

Table 5 presents the CAPEX, OPEX, and TAC. The CAPEX includes the cost of DCs, reactors, heat exchangers, liquid vessels, and vapour-liquid vessels. The capital cost is evaluated at 3371.8 × 10<sup>3</sup> US\$ and the operating cost is evaluated at 1464.7 × 10<sup>3</sup> US\$. For the production of 32 ktpy DMC, the TAC is 2523.7 × 10<sup>3</sup> US\$.year<sup>-1</sup>.

The profitability of the process is evaluated considering the following prices: DMC at 1000 US\$.tonne<sup>-1</sup> [23], urea at 247 US\$.tonne<sup>-1</sup> [24], and methanol at 445 US\$.tonne<sup>-1</sup> [25]. Overall, the cost of raw materials is 15325.5 × 10<sup>3</sup> US\$.year<sup>-1</sup> and the cost of heating and cooling utilities is 1464.7 × 10<sup>3</sup> US\$.year<sup>-1</sup>. Assuming a payback period of 3 years, the annualized capital cost is 1123.9 × 10<sup>3</sup> US\$.year<sup>-1</sup>, which amounts to about 35 US\$.tonne<sup>-1</sup> DMC.

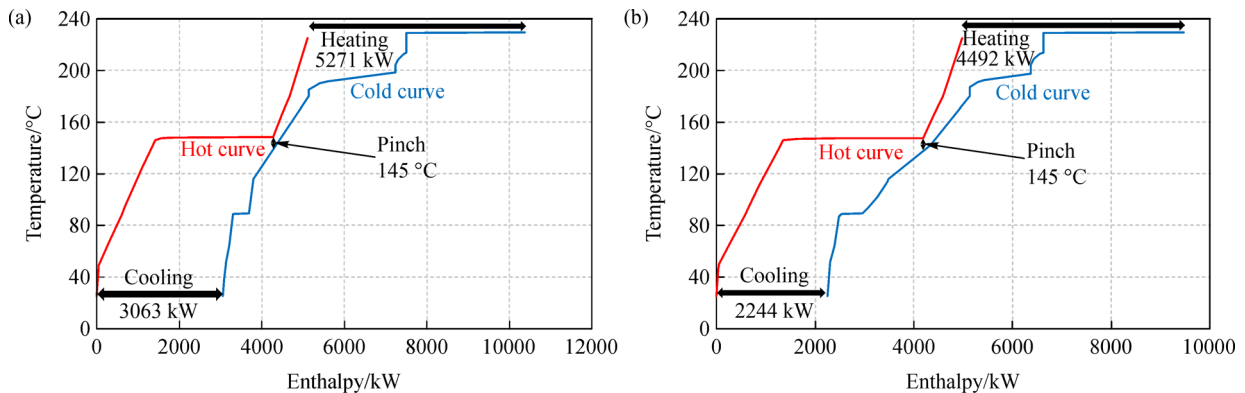


Fig. 5 Composite curves for heat integration: (a) without side reboiler and (b) with side reboiler.



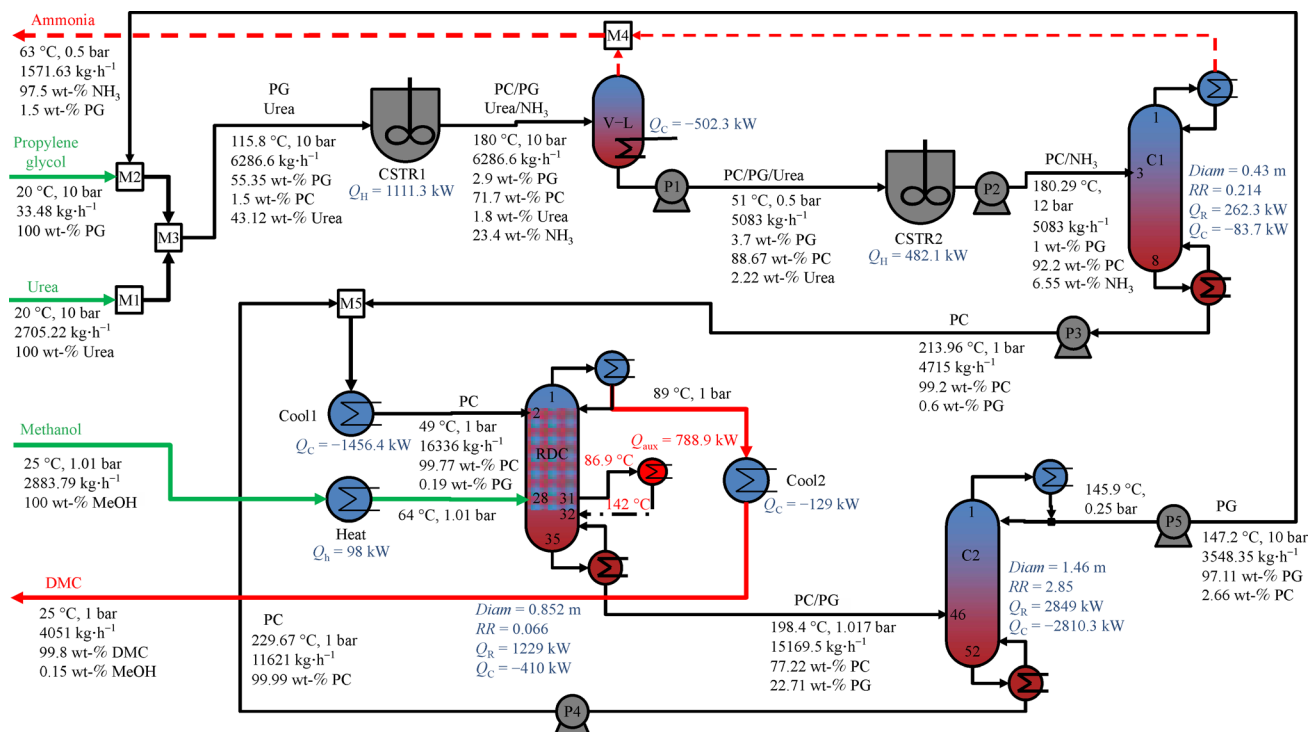


Fig. 6 Flowsheet of the DMC process, proposed for heat integration.

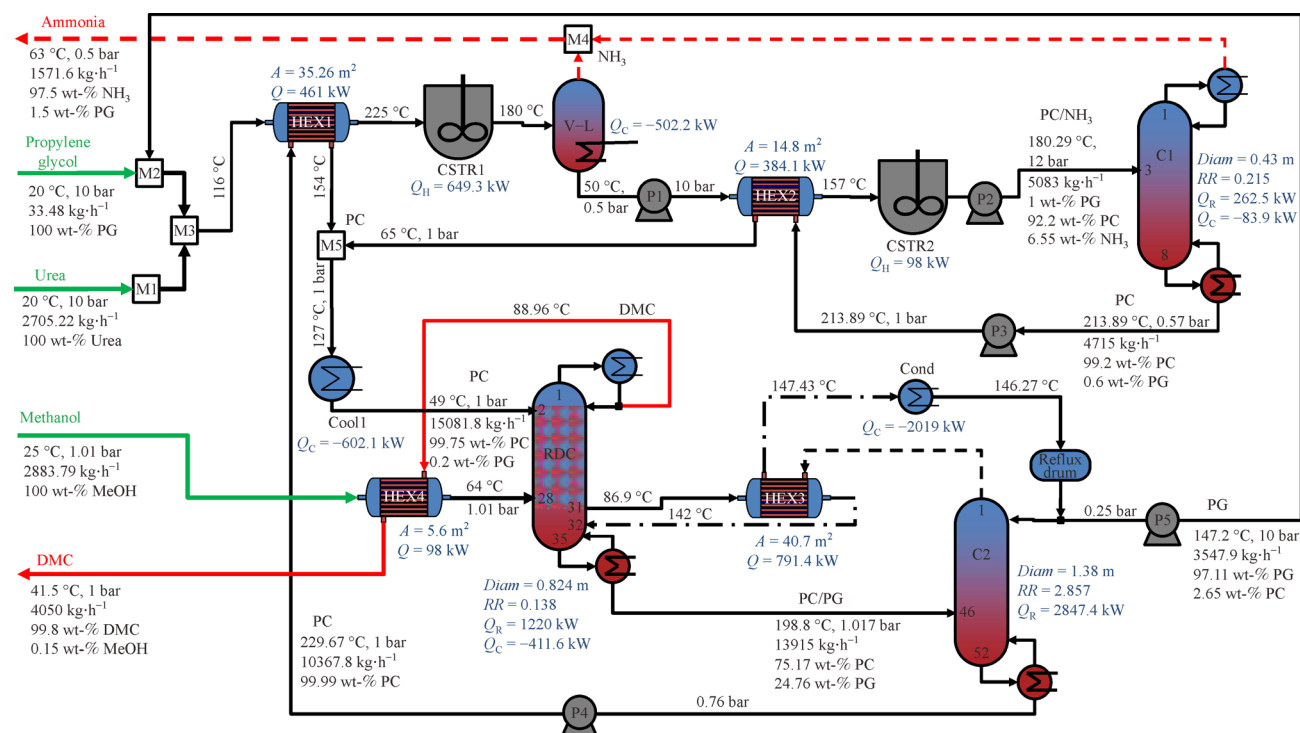
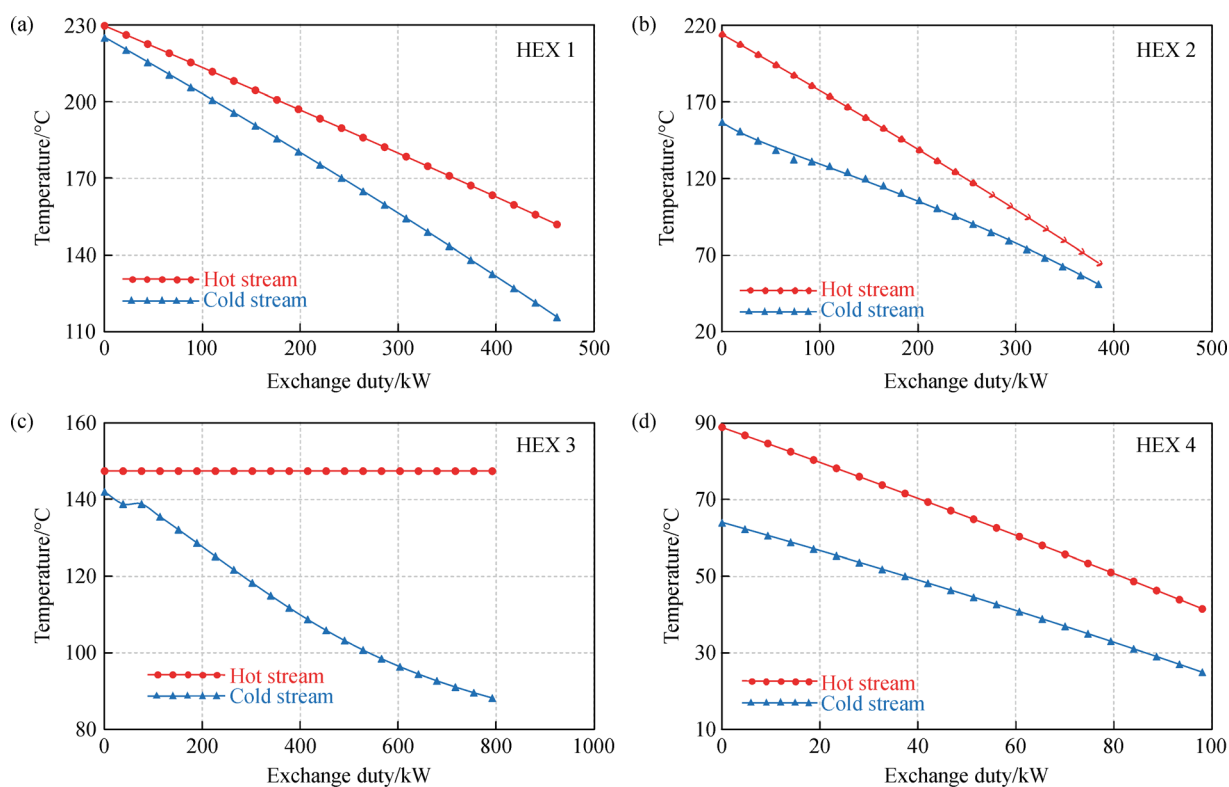


Fig. 7 Heat integrated process design for DMC production (HI-DC&RDC).

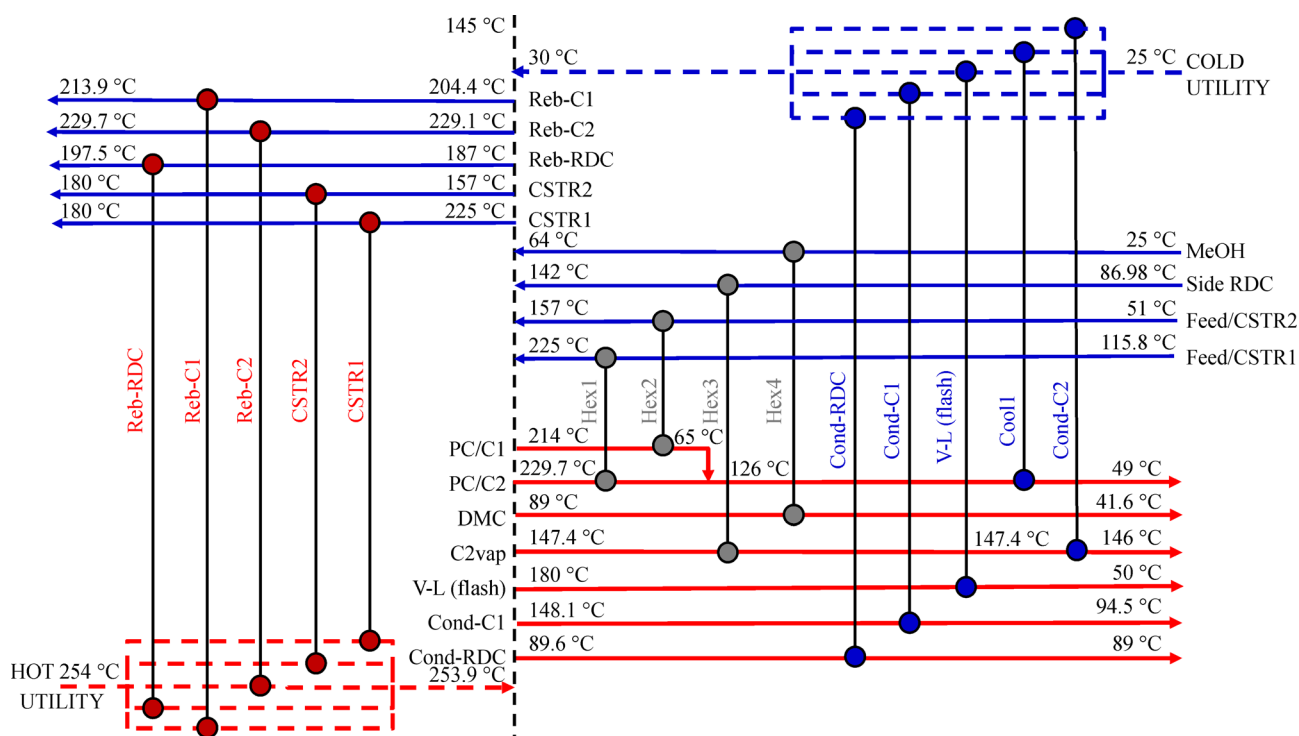
Thus, the total specific cost is 552.9 US\$·tonne<sup>-1</sup> DMC, which leads to an estimated profit of 447.1 US\$·tonne<sup>-1</sup> DMC (about 14500 × 10<sup>3</sup> US\$·year<sup>-1</sup>).

### 3.6 Sustainability metrics

The sustainability of the process can be evaluated using the



**Fig. 8** Temperature profiles of the heat exchangers (a) HEX1, (b) HEX2, (c) HEX3, and (d) HEX4.



**Fig. 9** Heat exchangers network for the heat integrated process.

**Table 4** Energy usage (heating requirements) in various scenarios for DMC synthesis and purification

Scenario		Energy balance					Total	Savings
Conv. DC	Unit	C1	C2	C3	C4	CSTR1&2		
	Energy/kW	237.3	5584.7	4722.8	3266.1	1585.1	15396	0%
Conv. HI-DC	Unit	C1	C2	C3	C4	CSTR1&2		
	Energy/kW	240.0	4790.6	714.4	3256.5	1585.5	10587	–31%
DC&RDC	Unit	C1	RDC	C2	Heat	CSTR1&2		
	Energy/kW	262.3	2100	2868.5	98	1593.4	6922	–55%
HI-DC&RDC	Unit	C1	RDC	C2	–	CSTR1&2		
	Energy/kW	262.5	1220	2847.4	–	747.3	5077	–67%

**Table 5** Economic evaluation of the process

Item description (unit)	C1	RDC	C2	CSTR1&2	HEX	Cool	Mixer	V-L	Total
Shell/(10 <sup>3</sup> US\$)	26.4	172.2	417.0	425.3	196.9	210.5	298.0	201.5	1947.8
Internals/(10 <sup>3</sup> US\$)	1.2	87.4	48.9	–	–	–	–	–	137.6
Condenser/(10 <sup>3</sup> US\$)	26.1	77.7	139.4	–	–	–	–	–	243.1
Reboiler/(10 <sup>3</sup> US\$)	87.6	190.3	570.7	–	–	–	–	–	1043.3
Heating/(10 <sup>3</sup> US\$·year <sup>–1</sup> )	58.8	347.3	810.2	173.4	–	–	–	–	1389.7
Cooling/(10 <sup>3</sup> US\$·year <sup>–1</sup> )	1.7	8.5	41.9	–	–	12.5	–	10.4	75.0
TAC/(10 <sup>3</sup> US\$·year <sup>–1</sup> )	107.7	531.7	1244.1	315.1	65.6	82.7	99.3	77.6	2523.7

following key metrics proposed by industrial experts [26]: material intensity, energy intensity, water consumption, toxic emissions, pollutant emissions, greenhouse gas (GHG) emissions—with lower values meaning better performance.

Material intensity expresses the mass of wasted materials per unit of output. Considering the inlet and outlet streams shown in the process flowsheet, it is clear that this process does not produce any waste. This is also confirmed by the calculations. The feed streams (inputs) consist of: urea = 2705.22 kg·h<sup>–1</sup>, methanol = 2883.79 kg·h<sup>–1</sup>, PG makeup = 33.48 kg·h<sup>–1</sup>. The products (outputs) are: DMC = 4050 kg·h<sup>–1</sup>, and NH<sub>3</sub> = 1571.6 kg·h<sup>–1</sup>. The waste amount is the difference of: inputs – outputs = 0.89 kg·h<sup>–1</sup>, thus leading to 0.89/4050 = 2.19 × 10<sup>–4</sup> kg<sub>waste</sub>·kg<sup>–1</sup> DMC (which is zero within the simulation tolerance).

Energy intensity represents the primary energy consumed per unit of output. The heat integrated process (described earlier) has heating requirements of 5077 kW (equivalent to 1.25 kW·h·kg<sup>–1</sup> DMC (or 4.5 MJ·kg<sup>–1</sup> DMC) and cooling requirements of –0.89 kW·h·kg<sup>–1</sup> DMC (or –3.2 MJ·kg<sup>–1</sup> DMC).

Water consumption expresses the amount of water used per unit of output. The temperature range from process to cooling tower is 10 °C, from 25 °C to 35 °C. The cooling capacity of water is then (per 10 K): 41.7275 kJ·kg<sup>–1</sup>. The flowrate is then derived from the cooling duty as follows: 3628.8 kW × 3600 s·h<sup>–1</sup>/41.7275 kJ·kg<sup>–1</sup> = 313.07 m<sup>3</sup>·h<sup>–1</sup>. As water cooling is obtained by evapora-

tion, this must be compensated by a make-up with fresh water. Following the 7% rule [26], the loss is 0.07 × 313.07 = 21.07 m<sup>3</sup>·h<sup>–1</sup>.

GHG emissions expresses the total GHG emitted per unit of output. The reductions in the cost of equipment and energy are also translated into lower CO<sub>2</sub> emissions associated to the energy use in the process. The CO<sub>2</sub> emissions associated to entire plant are estimated at 1750 kg·h<sup>–1</sup> (for a production capacity of 32 ktpy DMC). The GHG emitted per unit of output is 1750/4050 = 0.432 kg·kg<sup>–1</sup> DMC product. The total net carbon tax has been evaluated at 9.64 \$·h<sup>–1</sup> (84535.4 \$·year<sup>–1</sup>). The potential environment impact was evaluated in Aspen Plus using carbon tracking to calculate the CO<sub>2</sub> emissions. The fuel source considered is natural gas and the CO<sub>2</sub> emission factor data source used is the US Environmental Protection Agency Rule of ‘E9-5711’ (CO<sub>2</sub> E-US) proposed in 2009. The standard used for the GWP is USEPA (2009) with a carbon tax of 5 \$·ton<sup>–1</sup> CO<sub>2</sub>, a value which is easily upgradable to any particular year (carbonpricing-dashboards.worldbank.org).

### 3.7 Dynamic simulation and process control

In the DMC plant proposed in this work, the production process of PC is connected with the production of DMC. Both processes generate reactants for each other, while the PC and the PG are continually recycled. Preserving the correct ratio between reactants can be challenging in dynamics when recycling takes place from a process to

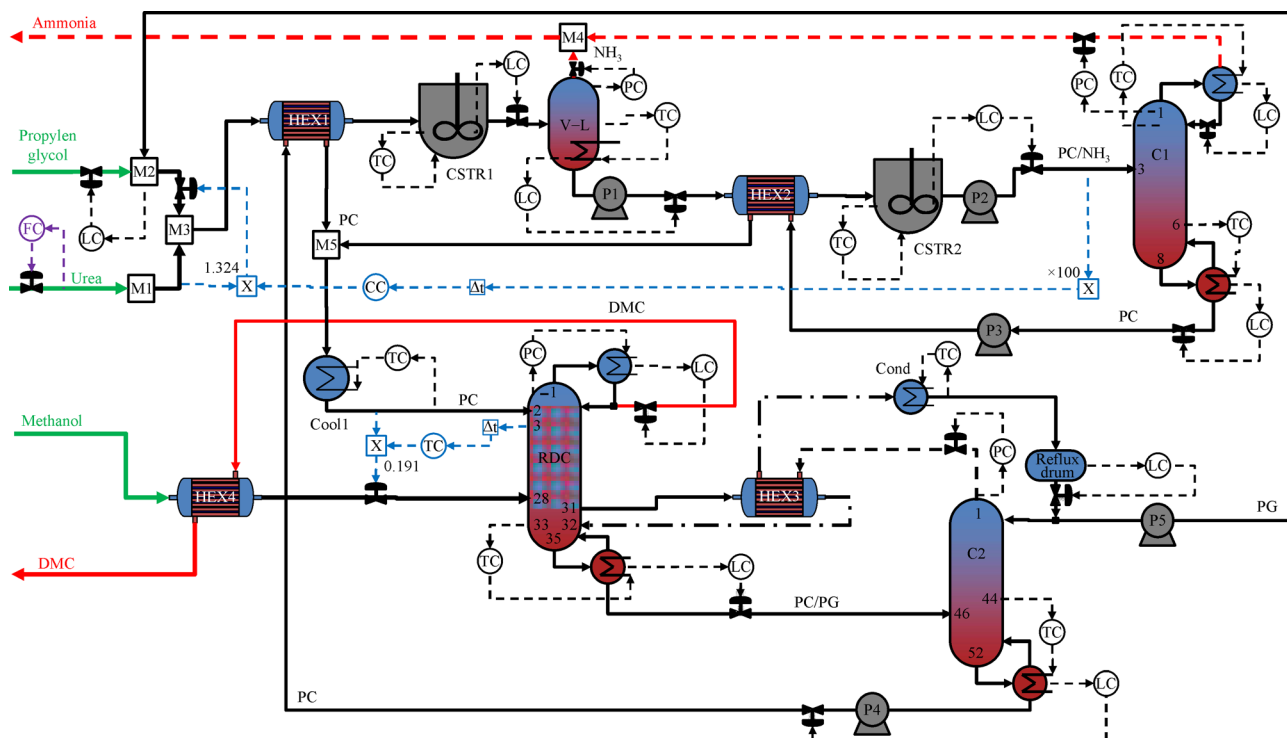


Fig. 10 Process control structure of heat integrated plant for DMC production.

Table 6 Controller tuning parameters

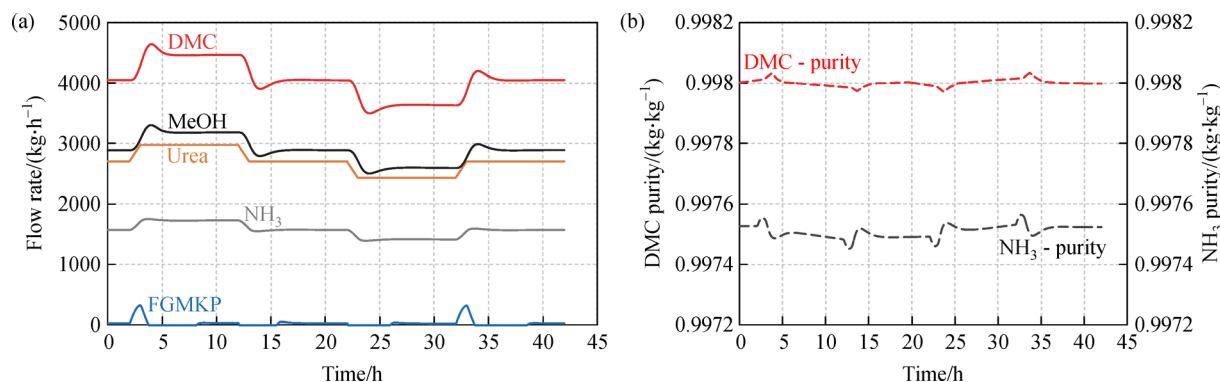
Controller	PV, value & range	OP, value & range	Kc/%	Time/min
FC urea	Flow rate = $2704 \text{ kg} \cdot \text{h}^{-1}$			
LC mix PGMKUP	Level = 1.875 m	Flow rate PGMKUP = $32.9 \text{ kg} \cdot \text{h}^{-1}$	130	13.2
	0–3.75 m	0–1000 $\text{kg} \cdot \text{h}^{-1}$		
Ratio control	Flow rate urea = $2704 \text{ kg} \cdot \text{h}^{-1}$	Flow rate propilen glicol = $3581 \text{ kg} \cdot \text{h}^{-1}$	1.324	
Concentration controller (CC) urea	Urea concentration = 1.429 wt-%	Urea:PG = 1.324	0.06	500
	0.04–0.24 wt-%	0–2.64		
TC CSTR1	Temperature = $180 \text{ }^{\circ}\text{C}$	Heat duty = $2.33 \text{ GJ} \cdot \text{h}^{-1}$	5	6
	$130 \text{ }^{\circ}\text{C}$ – $230 \text{ }^{\circ}\text{C}$	$-46$ – $46 \text{ GJ} \cdot \text{h}^{-1}$		
LC CSTR1	Level = 2.90 m	Product flow rate CSTR1 = $6285 \text{ kg} \cdot \text{h}^{-1}$	10	60
	0–4.14 m	0–12571 $\text{kg} \cdot \text{h}^{-1}$		
TC CSTR2	Temperature = $180 \text{ }^{\circ}\text{C}$	Heating duty = $0.35 \text{ GJ} \cdot \text{h}^{-1}$	5	6
	$130 \text{ }^{\circ}\text{C}$ – $230 \text{ }^{\circ}\text{C}$	$-7$ – $7 \text{ GJ} \cdot \text{h}^{-1}$		
LC CSTR2	Level = 2.90 m	Flow rate product CSTR2 = $5082 \text{ kg} \cdot \text{h}^{-1}$	10	60
	0–4.14 m	0–10164 $\text{kg} \cdot \text{h}^{-1}$		
TC flash V-L	Temperature = $50 \text{ }^{\circ}\text{C}$	Cooling duty = $-1.8 \text{ GJ} \cdot \text{h}^{-1}$	10	20
	$40 \text{ }^{\circ}\text{C}$ – $60 \text{ }^{\circ}\text{C}$	$-3.6$ – $0 \text{ GJ} \cdot \text{h}^{-1}$		
LC flash V-L	Level = 1 m	Product flow rate = $5082 \text{ kg} \cdot \text{h}^{-1}$	10	60
	0–2 m	0–10164 $\text{kg} \cdot \text{h}^{-1}$		
PC flash V-L	Column pressure = 0.5 bar	Vapor flow rate = $70.4 \text{ kmol} \cdot \text{h}^{-1}$	20	12
	0–1 bar	0–140 $\text{kmol} \cdot \text{h}^{-1}$		
PC C1	Column pressure = 0.5 bar	Vapor flow rate = $20 \text{ kmol} \cdot \text{h}^{-1}$	20	12
	0–1 bar	0–40 $\text{kmol} \cdot \text{h}^{-1}$		

(Continued)				
Controller	PV, value & range	OP, value & range	Kc/%	Time/min
LC reflux drum C1	Level = 3.35 m	Flow rate reflux = 339.8 kg·h <sup>-1</sup>	94	2.64
	0–4.8 m	0–679 kg·h <sup>-1</sup>		
LC sump C1	Level = 0.61 m	Bottom flow rate = 4714.9 kg·h <sup>-1</sup>	10	60
	0–1.22 m	0–9428 kg·h <sup>-1</sup>		
TC stage 1 C1	Temperature = 94.44 °C	Condenser duty = −0.301 GJ·h <sup>-1</sup>	10	20
	84 °C–104 °C	−1.89–0 GJ·h <sup>-1</sup>		
TC stage 6 C1	Temperature = 195.2 °C	Reboiler duty = 0.944 GJ·h <sup>-1</sup>	10	20
	185 °C–205 °C	0–1.89 GJ·h <sup>-1</sup>		
TC Cool1	Temperature = 49 °C	Cooler duty = −2.16 GJ·h <sup>-1</sup>	5	1
	39 °C–59 °C	−4.33–0 GJ·h <sup>-1</sup>		
Ratio control	Flow rate PC = 15084.2 kg·h <sup>-1</sup>	Flow rate metanol = 2884.38 kg·h <sup>-1</sup>	0.1912	
PC RDC	Column pressure = 1 bar	Condenser duty = −1.48 GJ·h <sup>-1</sup>	20	12
	0–2 bar	−2.96–0 GJ·h <sup>-1</sup>		
LC reflux drum RDC	Level = 1.37 m	Distillate flow rate = 4050.7 kg·h <sup>-1</sup>	10	60
	0–2.75 m	0–8099.8 kg·h <sup>-1</sup>		
LC sump RDC	Level = 1.43 m	Bottom flow rate = 13917.9 kg·h <sup>-1</sup>	10	60
	0–2.85 m	0–27830 kg·h <sup>-1</sup>		
TC stage 3 RDC	Temperature = 49.7 °C	PC:urea = 0.1912	0.0488	7.92
	40 °C–60 °C	0–0.38		
TC stage 33 RDC	Temperature = 149.79 °C	Reboiler duty = 4.39 GJ·h <sup>-1</sup>	10	20
	140 °C–160 °C	0–8.78 GJ·h <sup>-1</sup>		
PC C2	Column pressure = 0.25 bar	Top vapors flow rate = 178.56 kmol·h <sup>-1</sup>	20	12
	0–5 bar	0–357.05 kmol·h <sup>-1</sup>		
LC reflux drum C2	Level = 1.56 m	Condensate flow rate = 13665.38 kg·h <sup>-1</sup>	10	60
	0–3.12 m	0–27325.32 kg·h <sup>-1</sup>		
LC sump C2	Level = 1.875 m	Bottom flow rate = 10369.3 kg·h <sup>-1</sup>	10	60
	0–3.75 m	0–20734.25 kg·h <sup>-1</sup>		
TC condenser C2	Temperature = 145.97 °C	Condenser duty = −7.27 GJ·h <sup>-1</sup>	10	20
	135 °C–155 °C	−14.53–0 GJ·h <sup>-1</sup>		
TC stage 44 C2	Temperature = 179.66 °C	Reboiler duty = 10.25 GJ·h <sup>-1</sup>	10	20
	170 °C–190 °C	0–20.5 GJ·h <sup>-1</sup>		

another. Moreover, heat integration may cause inflexibility in process control. The plantwide control structure is given in Fig. 10, while the controller tuning parameters are listed in Table 6. The basic control ensures pressure and level controls for the DCs and temperature and liquid levels controllers for the reactors. The most thermally sensitive stages of the DCs are chosen for temperature control, by manipulating the reboiler. The reflux ratio of all DCs is fixed. The temperature of the flash vessel and of the PC stream fed in the RDC is controlled by manipulating the cooling duty of the V-L unit and Cool1, respectively. The DMC production rate is given by the fresh urea flow rate, which is the throughput manipulator. According to the

overall stoichiometry and neglecting the loss of reactants,  $1 \text{ kmol} \cdot \text{h}^{-1}$  of urea needs  $2 \text{ kmol} \cdot \text{h}^{-1}$  MeOH to react with. To achieve this, the temperature in the top of RDC is used to detect any imbalance (too much/less MeOH leads to an increase/decrease of temperature) and a temperature controller (TC stage 3 RDC) compensates this by changing the ratio between MeOH and PC fed to RDC.

This ensures that the right amount of MeOH is brought into the process. Similarly, the ratio between PG and urea fed to CSTR1 is kept constant (value given by the CC urea), which ensures that the PG makeup compensates the losses. Compared to the time scale of the process, the sensors were considered to be fast, hence their dynamics



**Fig. 11** Dynamic results for 10% disturbances in urea feed flow rate: (a) change in flowrates and (b) change in DMC and NH<sub>3</sub> purities.

were neglected, with two exceptions. The temperature measurement placed in the reactive section of the RDC may be somehow slow because it is not completely immersed in a liquid phase, therefore it included one-minute dead-time. Additionally, one-minute dead-time and one-minute sampling period were specified for the concentration sensors. For most controllers, the default Aspen Plus settings were used. However, it was found that tighter control is needed for the level in the reflux drum of the C1 (due to the interaction between pressure, temperature and level control loops) and for the level in the PG mixing vessel (which is a measure of PG + PC inventory). For the temperature and concentration loops involving measurement dead-time, the stability limit was found by the auto tuning variation method, and the controller parameters were set according to the Tyreus-Luyben rules [21].

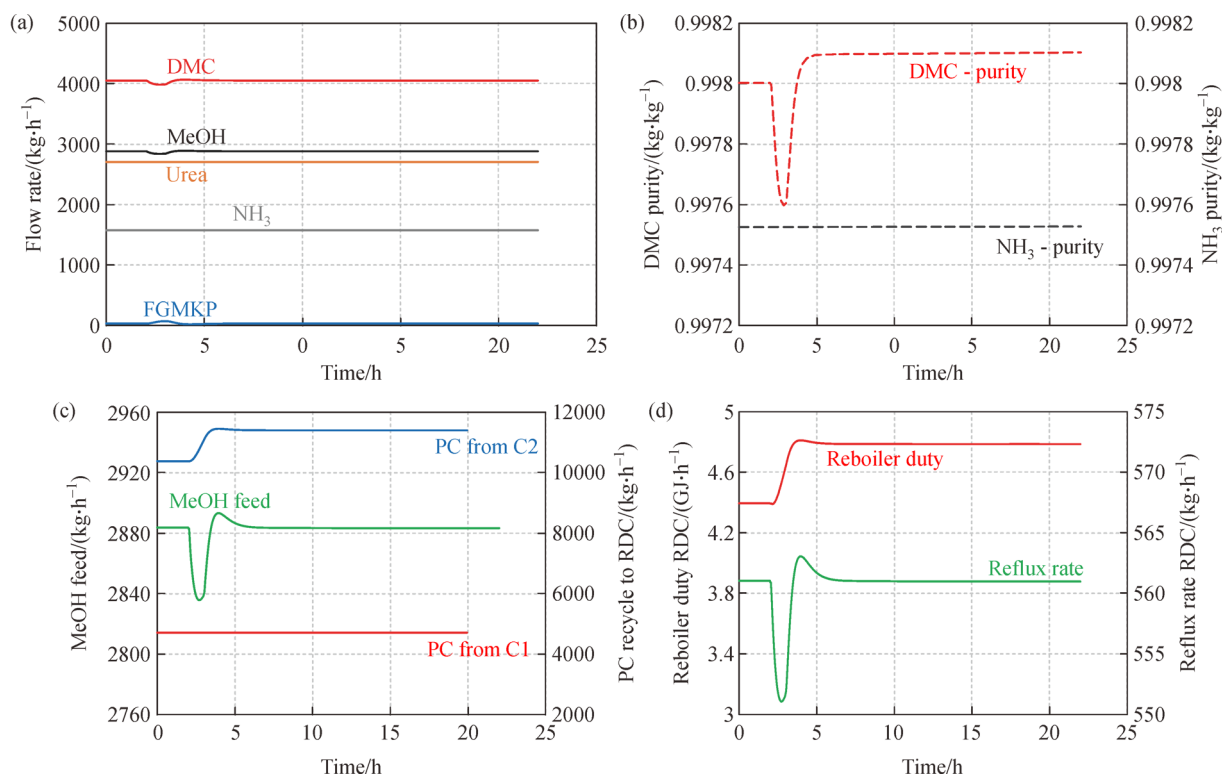
The performance of the control structure is given in Fig. 11 for  $\pm 10\%$  production changes. After 2 h of steady-state operation, the urea flow rate is increased by 10% as 1 h ramp. The CC ensures that all urea is consumed by adjusting the urea:PG ratio. A small amount of PG makeup is necessary. The temperature controllers of the V-L flash unit and stage 6 from C1 ensure that the entire amount of NH<sub>3</sub> produced is removed from the process. The PC:MeOH ratio controller notices that the PC stream flow rate increases and acts by adding more MeOH. The feedback for the PC:MeOH ratio controller is the temperature on stage 3 in RDC which drops when more PC is fed and increases when less PC is fed. When the temperature decreases on this stage, it means that there is lack of methanol in the top of the column and its flow rate must be increased in order to maintain the DMC purity. The process stabilizes within 5 h and the DMC purity is almost unchanged. When the urea flow rate was reduced by 10% (time = 22 h), the urea:PG controller ratio fed less PG to CSTR1. The temperature of stage 3 in RDC increases, and the methanol stream flow rate is reduced. Remarkably the DMC purity is maintained at desired specifications while changing the production rate by  $\pm 10\%$ . As

previously discussed, the kinetics used for process design might not represent well the actual reaction rate, as the simulation uses values of the reaction rate and equilibrium constants that were determined at 313 K, while the temperature in the reactive section of the column is higher. The most unfavourable situation is when the forward reaction ( $\text{PC} + 2\text{MeOH} \rightarrow \text{PG} + \text{DMC}$ ) has a small activation energy (thus, its rate does not increase significantly with temperature) and the reaction is exothermal (thus, the equilibrium constant decreases with the temperature). For this reason, a dynamic simulation was performed, the rate of reverse reaction ( $\text{PG} + \text{DMC} \rightarrow \text{PC} + 2\text{MeOH}$ ) is increased by a factor 1.8 (see “Chemistry and kinetics” section), corresponding to a decrease of the equilibrium constant by the same factor.

The results of dynamic simulation are shown in Fig. 12. After 2 h of steady state operation, the rate constant of the reverse reaction is changed as a one-hour ramp. The top-left plot shows the plant inlet and outlet streams. As the production rate is given by the fresh urea flow rate, the flow rates of DMC and NH<sub>3</sub> products are practically unchanged, and the flow rate of fresh methanol matches the flow rate of fresh urea. Moreover, the DMC and NH<sub>3</sub> purities are not affected (top-right plot). However, the disturbance affects the flows internal to the part of the plant where DMC is produced (bottom-left plot). The flow rate of MeOH fed to the RDC temporarily decreases. The bottom stream (PC/PG) contains more unreacted PC, which is separated in column C2 and recycled. The reboiler duty increases, in order to avoid contamination of the bottom stream with light species. As the reflux ratio is constant, the reflux follows the change of the distillate rate (bottom right plot). Results shown in Fig. 12 demonstrate that, despite the rather large disturbance, the control structure is able to ensure stable operation, a new steady state being reached quite fast, and maintained.

Other possible disturbances are impurification of the feed streams. In case of methanol, the most likely impurity is water, which will contaminate the DMC product as the separation PG/water is easy. The light impurities present in





**Fig. 12** Dynamic simulation results for change of the  $\text{PG} + \text{DMC} \rightarrow \text{PC} + 2\text{MeOH}$  reaction rate constant (ramp up from 0.0021 to  $0.0038 \text{ kmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ , at  $t = 2 \text{ h}$ ): (a) change in flowrates; (b) change in DMC and  $\text{NH}_3$  purity; (c) change in MeOH and PC flowrates; (d) change in reboiler duty and reflux rate.

the urea feed (e.g., free  $\text{NH}_3$  0.5%, free water 0.5%, biuret max 1%) will be found in the vapor distillate of column C1.

## 4 Conclusions

The DMC synthesis by indirect alcoholysis of urea, using an excess of PC instead of methanol, can offer key advantages in terms of economic and sustainability metrics. A process combining a continuous CSTR reactor system to obtain PC and a RDC for the synthesis of DMC was proven to be feasible. Overall, it brings several advantages such as less equipment, elimination of the methanol/DMC azeotrope recycle, as well as significant energy and cost savings.

The RDC takes advantage of the synergistic effects of combining reaction and distillation into a single unit and it brings 34.6% energy savings. In addition, the heat integration allows another 17.4% energy savings, thus giving a total of 52% energy savings as compared to the conventional process. As a result, the energy requirement in this improved DMC process based on RD is reduced from  $2.64 \text{ kW} \cdot \text{h} \cdot \text{kg}^{-1}$  DMC (or  $9.5 \text{ MJ} \cdot \text{kg}^{-1}$ ) in the conventional RSR system, to only  $1.25 \text{ kW} \cdot \text{h} \cdot \text{kg}^{-1}$  DMC (or  $3.95 \text{ MJ} \cdot \text{kg}^{-1}$ ). This value is drastically lower than that of all other DMC processed (listed in Table 1).

In economic terms, the operating cost is reduced to

$1464.7 \times 10^3 \text{ US\$} \cdot \text{year}^{-1}$  and the cost of the equipment is reduced to  $1123.9 \times 10^3 \text{ US\$}$ , giving a *TAC* of only  $2523.7 \times 10^3 \text{ US\$} \cdot \text{year}^{-1}$  (for a plant capacity of 32 ktpy DMC), which represents savings of 46% as compared to the conventional RSR process. Despite the complexity, the proposed process can run safely and can handle  $\pm 10\%$  changes in the production rate (while maintaining the DMC product quality on-spec), by applying basic controllers (level, temperature, and pressure) and two ratio controllers to ensure the stoichiometry for the reactions.

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