



# Simultaneous Synthesis of Heat Exchanger Network and Process Optimization for Dimethyl Carbonate Production

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Dimethyl carbonate (DMC), an important environmentally benign chemical because of its biodegradability and less toxicity, is widely used in process industry. A reactive-distillation-based process was recently developed by Liaoning Oxiranchem Group to produce DMC via transesterification of methanol (MeOH) and ethylene carbonate (EC), coproducing ethylene glycol (EG). To synthesize the heat exchanger network (HEN) of the preliminary process design, it was noticed that the variation of operating conditions of the high pressure column in the pressure swing distillation scheme had strong impacts on the temperature and composition of the overhead stream, and thus affected the HEN design. Taking into consideration the strong interaction between the process units and HEN, the process operating conditions were optimized simultaneously with the synthesis of HEN, instead of using the traditionally sequential optimization scheme. Based on Pinch technology, the Composite Curves and Grand Composite Curves were used to dig out the potential for the reduction of energy consumption. Sensitivity analysis was carried out to investigate how the operating variables affect the energy targets of the HEN. By assessing and comparing the energy target in each case, the optimal operating condition was obtained, under which the heat duties of hot utility and cold utility were 3.84 MW and 3.45 MW respectively. The comparison between the proposed HEN design and the one acquired using the sequential optimization approach showed a considerable reduction of 20.8 % in the hot utility consumption, indicating that through simultaneous optimization of process operating conditions and HEN synthesis, more energy savings could be expected.

## 1. Introduction

Dimethyl carbonate (DMC), as a versatile compound, possesses properties of no toxicity and biodegradability that make it a true green reagent to be used in syntheses. In many aspects, DMC is an environmentally benign building block by using which the pollution can be prevented at the source (Ono, 1997). Under strict laws and regulations of environmental protection, DMC is used increasingly in the chemical industry in the past few years as a substitute for toxic substance, such as dimethyl sulphate and phosgene (Zhang et al., 2015).

The traditional way to produce DMC used highly toxic phosgene as raw material (de Groot et al. 2014), but nowadays the reaction routes utilizing CO<sub>2</sub> have attracted substantial research efforts in recent years since it offers direct benefits to the environment while creating valuable products from the emitted and undesired CO<sub>2</sub>. Especially, the ethylene carbonate (EC) route is the most promising process alternative in terms of atom efficiency, energy consumption and net CO<sub>2</sub> emission (Kongpanna et al., 2015). By a transesterification reaction of methanol (MeOH) with EC, DMC can be produced, together with another useful by-product, ethylene glycol (EG). To achieve a complete conversion of EC, a reactive distillation (RD) column can be employed with MeOH in excess. However, the azeotrope of MeOH and DMC will be distilled from the top of the RD column as the azeotropic temperature is the lowest of the system, making the separation of the mixture more complicated.

Wang et al. (2010) conducted both steady-state and dynamic simulations on a plant-wide RD-based design of DMC synthesis process and found that the extractive distillation was more economical than the pressure-swing distillation (PSD). But it should be noted that the conclusion was drawn without taking into consideration heat integration, which is one advantage of PSD. Hsu et al. (2010) found aniline to be a very effective entrainer for

the extractive distillation process and proposed overall control strategy of the RD process. Choomwattana et al. (2016) developed a coproduction process of DMC and EG from biomass and designed the heat exchanger network (HEN) for the overall process. However, the strong interaction between the process units and HEN was completely ignored.

Heat integration plays an important role in enhancing energy efficiency and operating costs. Traditionally, the process optimization and the design of HEN are performed sequentially, that is, the process is optimized in the first stage to identify the optimal operating conditions, and then heat integration is conducted as the second stage based on the stream information. Although the decomposition of the overall optimization procedure into sub-problems makes it easier to solve, this approach may not fully optimize the whole process and may overestimate the utility cost. To overcome the drawback, Duran and Grossman (1986) proposed a simultaneous optimization strategy by adding a set of heat integration constraints that predict the minimum utility targets to the process optimization model. With the combined synthesis problem formulated as a mixed-integer nonlinear programming (MINLP) problem, Drobez et al. (2012) performed the process design simultaneously with HEN synthesis on a biogas process, and Ahmetovic and Kravanja (2013) presented a novel superstructure and optimization model for the simultaneous synthesis of process water network and HEN. Kong et al. (2016) proposed an optimization framework for process synthesis with simultaneous heat integration and utility plant design. It is proved that the simultaneous optimization approach can achieve higher profit and lower operating cost than the sequential approach (Psaltis et al., 2016).

The aim of this research is to simultaneously synthesize the HEN and identify the optimal operating conditions of a DMC production process which is developed by Liaoning Oxiranchem Group. To simplify the analysis, commercial software tools are utilized to carry out process simulation and heat integration, such as Aspen Plus, Aspen Energy Analyser and Excel.

## 2. Process Modelling

### 2.1 Process description

A plant-wide process for producing DMC and coproducing EG by the transesterification of MeOH and EC was developed by Liaoning Oxiranchem Group, as shown in Figure 1. The flowsheet consists of 5 columns, including one reactive distillation column (D1) where the transesterification reaction occurs, and 4 distillation columns (D2 – D5) for separation. Fresh MeOH with a flowrate of 56 kmol/h and EC with a flowrate of 28 kmol/h are fed to D1 separately. A homogeneous catalyst is solved in EC. The overhead product of D1 is a mixture of MeOH and DMC near the azeotropic composition, fed to a PSD system consisting of a high-pressure column (D2) and a low-pressure column (D3). Both the distillate products of D2 and D3 are MeOH/DMC mixture at approximate azeotropic composition under operating pressure. The former one is recycled to D1 for further reaction, and the latter one is recycled to D2 for further separation. DMC product (99.9 wt %) is withdrawn from the bottom of D3. EG and a small amount of unreacted MeOH are withdrawn from the bottom of D1 and fed to D4 for further separation. Recovered MeOH is distilled from the top of D4 and then recycled to D1 for further reaction. D5 is a finishing column in case of the impurity of EG, in which EG is withdrawn from the side stream with other light components being distilled from the top and catalysts being recovered from the bottom of D5 for subsequent processing. Table 1 lists the specifications of all columns.

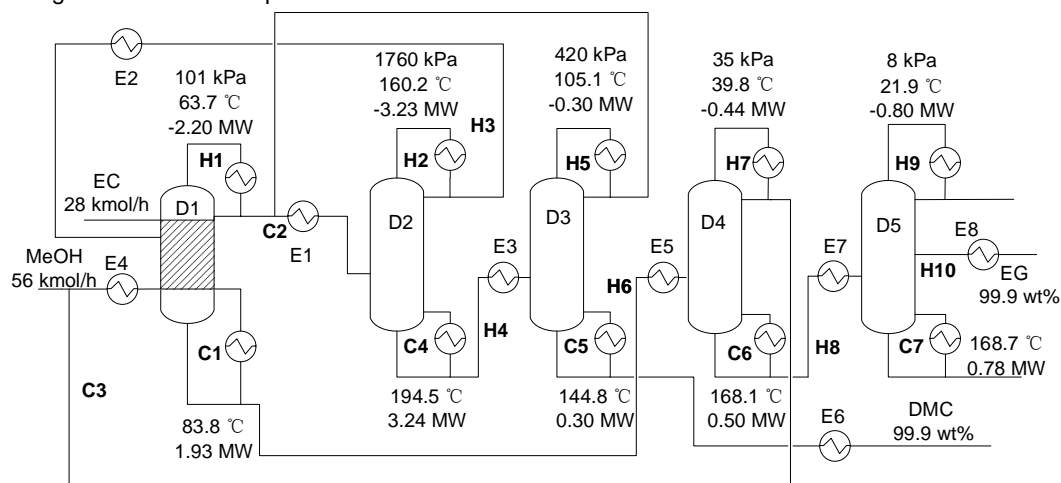


Figure 1: Process flow diagram of the DMC production process

By examining the process carefully, it was noticed that the pressure of D1 was predetermined according to experimental data provided by Liaoning Oxiranchem. D4 and D5 are vacuum columns to ensure the temperatures of the bottom products can be satisfied using the existing utilities. The pressure of D3 is identified to ensure the purity of DMC product. Only the pressure of D2 can be varied, which offers a degree of freedom to optimize the process. It is known that the mass fraction of MeOH in the MeOH/DMC azeotrope increases when the pressure goes up. Thus, the higher the pressure of D2, the higher purity of MeOH in the distillate product, which will further affect the performance of D1 when recycling to the RD column. Also, the higher temperature of D2 distillate might provide more potential for heat integration. Besides, it was observed that while the flowrates of all other streams are determined by mass balances and the specifications listed in Table 1, the distillate rate of D2 can be varied and consequently will impact the performance of D1 since it is a recycle stream. In summary, the pressure and the distillate rate of D2 are two degrees of freedom in process design, not only influencing the performance of the RD column and the whole process, but also the heat integration as a result. Thus, the operating conditions and HEN must be optimized simultaneously without ignoring the strong interactions between them.

Table 1: Specifications of columns

Column	Specifications
D1	Conversion of EC, $\geq 99.6\%$ ; DMC in bottom product $\leq 0.2\%$
D2	Distillation of the column, DMC/MeOH azeotrope under operating pressure
D3	Product purity of DMC $\geq 99.7\%$ , Productivity $\geq 2,400$ kg/h
D4	Recovery ratio of MeOH, $\geq 99.0\%$
D5	Product purity of EG $\geq 99.9\%$ , Productivity $\geq 1,700$ kg/h

## 2.2 Kinetic and thermodynamic models

The transesterification reaction of EC and MeOH is processed as Eq(1). The kinetic equation for the reaction catalyzed by a homogeneous catalyst is expressed as Eq(2), where  $r_{EC}$  is the reaction rate of EC (mol/(L min)) and  $C_i$  is the concentration of the  $i$  component (mol/L). UNIQUAC activity coefficient model for the liquid phase and the Redlich-Kwong equation of state for the vapor phase were used for phase equilibrium calculation, and the model parameters were taken from Hsu et al. (2010).



$$r_{EC} = 1.3246 \cdot \exp\left(-\frac{13,060}{RT}\right) \cdot C_{EC} \cdot C_{MeOH} - 15,022 \cdot \exp\left(-\frac{28,600}{RT}\right) \cdot \frac{C_{EG} \cdot C_{DMC}}{C_{MeOH}} \quad (2)$$

## 2.3 Analysis methods and tools

Sophisticated software tools were used to carry out this study. The process design was conducted in commercial simulators Aspen Plus, in which rigorous models are employed for the calculations of unit operations and thermodynamic calculations. Heat integration was modelled in Aspen Energy Analyser which can predict the minimum utility target and heat exchanger area target based on Pinch technology when provided with stream and equipment conditions. The output data of Aspen Plus and the input data of Aspen Energy Analyser were externally linked using Excel where optimization solver could be integrated. However, to simplify the problem in this research, a sensitivity analysis was performed instead of complicated optimization for a preliminary process design and HEN synthesis.

## 3. Results and analysis

The existed process flowsheet developed by Liaoning Oxiranchem Group was evaluated as the base case, in which the column pressure of D2 was 1,960 kPa, and the distillate rate was 5,300 kg/h.

### 3.1 Sensitivity analysis of the operating pressure of D2

Taking into consideration the economic efficiency of the equipment, the pressures ranging from 1,160 kPa to 2,160 kPa were investigated. As shown in Figure 2(a), when the pressure of D2 increases, the mass fraction of MeOH in the distillate of D1 goes up because of increased azeotropic composition. The condenser duty of D2 is decreased because of a lower enthalpy of phase change of MeOH than DMC. However, the reboiler duty changes little while the specifications of all columns have been satisfied. On the one hand, the increase in the temperature of D2 favours heat integration. On the other hand, the decrease in the condenser duty leads to reduced heat recovery. Therefore, an optimal operating pressure exists.

The same conclusion can be drawn if the temperature-enthalpy curve is observed carefully. As marked in Figure 3(a), the pinch for the hot stream is always located at the turning of the curve no matter under what operating pressure. However, the pinch for the cold stream moves up gradually from a to b as the pressure rises, which can be seen in Figure 3(b). Figure 3(c) clearly shows that as the temperature of D2 increases, the pinch temperature moves up that makes the cold and hot curves closer to each other to achieve better heat recovery. But in the meantime, the right end of the hot curve becomes far away from the right end of the cold stream due to the variations in the stream compositions and flowrates. As a result, indicated by the Figure 3(d), the minimum consumption of hot utility is decreased at the beginning and then increased. The most appropriate operating pressure is 1,760 kPa.

### 3.2 Sensitivity analysis of the distillate rate of D2

The distillate rate of D2 ranging from 4,400 kg/h to 5,600 kg/h was examined. It is illustrated in Figure 2(b) that as the distillate rate increase, the mass fraction of MeOH in the distillate of D2 increases at first and then decreases, while that in the distillate of D1 slightly goes up. Because more product is withdrawn from the top of the column, both the condenser duty and the reboiler duty of D2 are increased. The less existence of MeOH in the bottom product of D2 makes the temperature of the reboiler rise, as circled in Figure 4(a). To satisfy the specifications of all columns, the operating conditions of each column were adjusted in each simulation, which led to changes in the stream compositions, flowrates and enthalpies. As a result, both the right ends of the Hot Composite Curve and the Cold Composite Curve move to the right simultaneously. Figure 4(b) reveals that as the distillate rate goes up, the minimum consumption of hot utility decreases at the beginning and then increases. The most appropriate distillate rate is found to be around 5,000 kg/h, with the minimum utility consumption.

### 3.3 Optimal process operating conditions and HEN synthesis

Since the cold utility, in this case, is cooling water which is much cheaper than steam, it is more meaningful to focus on the energy target of hot utility. Figure 5 illustrates how the operating pressure and distillate rate of D2 affect the minimum hot utility consumption of the whole process. The comparison between the results of sequential approach and that of simultaneous approach is listed in Table 2. In the sequential approach, HEN was synthesized after the operating conditions were determined, which were 1,960 kPa as the pressure and 5,300 kg/h as the distillate rate of D2. In the base case, the energy targets of hot utility and cold utility are 4.85 MW and 4.39 MW respectively. However, using a simultaneous approach which optimizes the operating conditions and the HEN design at the same time, the minimum consumption of hot and cold utility are 3.84 MW and 3.45 MW, reducing by 20.8 % and 21.5 %, respectively. Finally, an optimal HEN design with minimum energy consumption is shown in Figure 6, in which the distillate vapour of D2 is used to heat several other streams for maximum heat recovery.

Table 2: Comparison between the sequential approach and the simultaneous approach

	Pressure of D2 / kPa	Distillate of D2 / kg·h <sup>-1</sup>	Hot Utility Target / MW	Cold Utility Target / MW
Sequential approach	1,960	5,300	4.85	4.39
Simultaneous approach	1,760	5,000	3.84	3.45
Reduced by	N/A	N/A	20.8 %	21.5 %

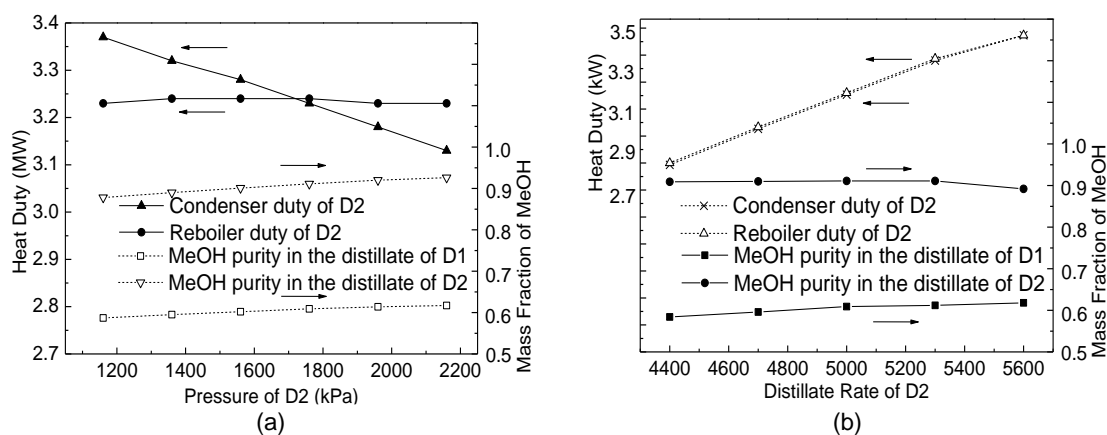


Figure 2: Effects of (a) pressure of D2 and (b) distillate rate of D2 to the heat duty of D2 and the purity of MeOH

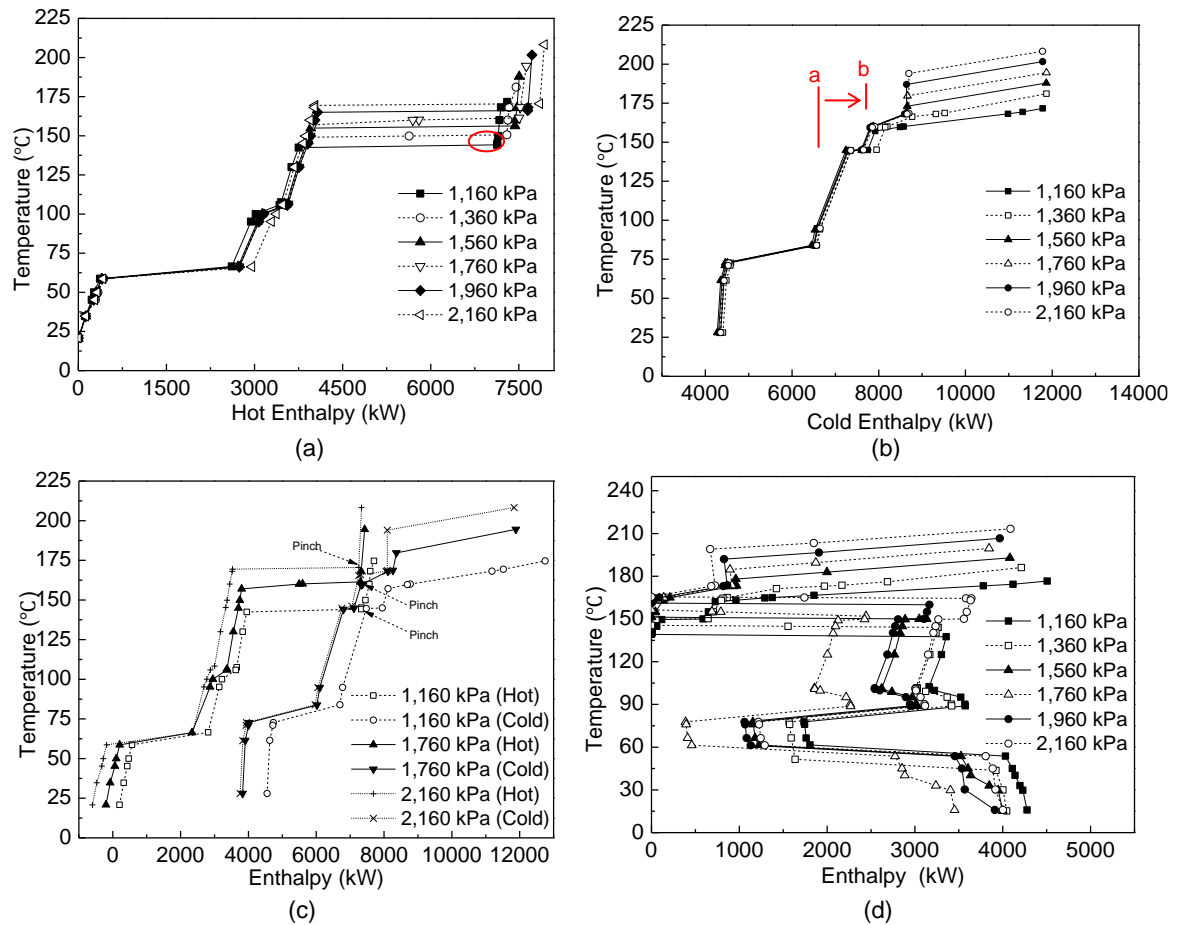


Figure 3: (a) Hot Composite Curves, (b) Cold Composite Curves, (c) Pinch locations and (d) Grand Composite Curves at different pressures of D2

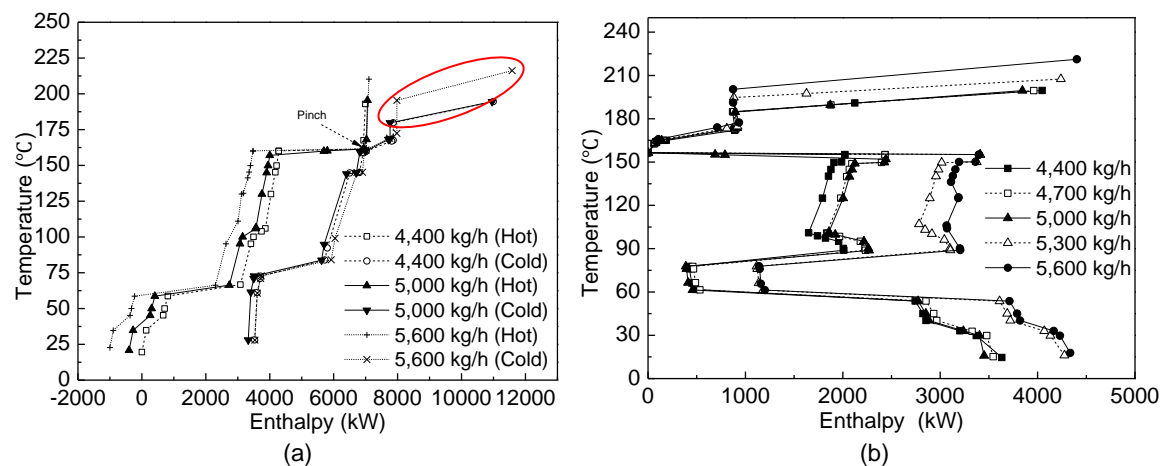


Figure 4: (a) Pinch locations and (b) Grand Composite Curves at different distillate rates of D2

#### 4. Conclusion

This paper synthesized the heat exchanger network simultaneously with the optimization of the operating conditions of a reactive-distillation-based DMC production process developed by Liaoning Oxiranchem Group. Using Aspen Plus for steady state simulation, Aspen Energy Analyser for the analysis of energy targets of heat exchanger network and Excel to externally link the two software tools, a sensitivity analysis was carried out to

investigate how the operating conditions affected the process performance and the heat integration. Based on the analysis results, the optimal operating conditions were found with minimum energy targets. Compared with the traditional sequential approach, the simultaneous approach shows overwhelming advantages by reducing the overall utility consumption by more than 20 %.

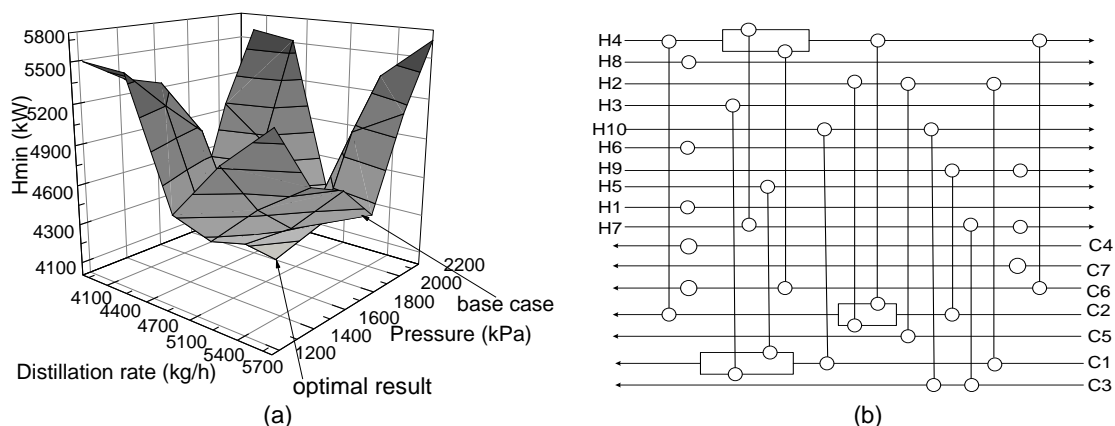


Figure 5: (a) The minimum consumption of hot utility under different operating conditions and (b) optimal HEN design fulfilling the energy targets

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