Process Optimization of Coke Oven Gas to Methanol Based on the Downgrade of By-Product Steam

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Abstract

In the coke oven gas to methanol (CTM) process, boiling water (above 200 °C) is generally used as the coolant in the methanol synthesis reactor, and thus, medium-pressure steam is generated as a by-product. In this paper, the influence of the coolant temperature on the CTM process is investigated from two aspects, which are the performance analyses of the reactor and the overall process and the energy integration of by-product steam. The results reveal that the coolant temperature plays a key role in the CTM process optimization. When the coolant temperature is reduced to 187 °C, though low-pressure steam is generated, the techno-economic performance of the whole process is greatly improved: the energy/exergy efficiency is increased by 4–9%, energy cost is saved by 37.1%, income is increased by 5.4 M\$/year, and the CO₂ emission is reduced by 21.3%.

Keywords Coke oven gas · Methanol synthesis · Process optimization · Energy saving

Introduction

Coke oven gas (COG) is a by-product of coal carbonization process, and it mainly comprises H₂ (55–60 vol%), CO (5–8 vol%), CO₂ (3–6 vol%), CH₄ (23–27 vol%), and other impurities (e.g., N₂ and H₂S) [1, 2]. On average, 1.25–1.65 tons coal can produce 300–360 m³ of COG [3]. China, as the biggest country of coke production in the world, produced approximately 210 billion m³ of COG at present [4, 5]. However, only half of the COG was utilized as fuel; the rest was directly emitted after burning, resulting in huge energy waste and serious environmental pollution [2, 6]. Nowadays, COG is utilized in several processes such as methanol synthesis, hydrogen production, and power generation [7–11], and many are still under research [12–16]. By comparison, COG to methanol (CTM) process is an established technology that has been widely accepted since its industrialization in 2004 [17, 18]. Wang [19] evaluated and compared four avenues of utilizing COG: methanol synthesis, power generation, hydrogen production, and direct reduced iron production, and the result showed that methanol synthesis has the advantages of low costs and low pollutant emissions.

To further increase utilization and reduce cost, CTM process still needs to be optimized [20]. Qian et al. [21] presented an integrated process of COG tri-reforming and coal gasification to methanol, in which the energy efficiency and CO₂ usage of the co-feed process were increased by about 10% and 25% compared to the conventional CTM process. Yi et al. [22] proposed a new concept which involves integrating CTM process with CO₂ recycle (CTMR) and compared with the conventional CTM process, energy efficiency was increased by 9%, and CO₂ emission was reduced by 62%. Gong et al. [23] designed a CTM process integrated with CO₂ recycle and H₂ separation, and compared with CTMR, energy efficiency was increased by 8.2% and CO₂ emission was reduced by 23%. Wu et al. [24] optimized the temperature of the reactor and H₂O/(CO₂ + CO + CH₄) ratio of the reforming unit in industrial CTM process, and the methanol yield was improved by 3–4%. Moreover, Manenti et al. [25], Shahrokhi and Baghmisheh [26] studied the methanol synthesis reactor and found that the coolant temperature strongly affects the methanol production and reactor thermal stability. Manenti et al. [27, 28] reported that high coolant temperatures are harmful to the catalyst and have an unfavorable effect on the thermodynamic equilibrium, which hinders the methanol synthesis, while low temperatures limit the reaction kinetics and thus impede the methanol synthesis. Bozzano and Manenti [29] noted that several studies considered only single unit or part of the methanol synthesis process. However, few related studies have reported

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the effects of the reactor coolant temperature on the overall CTM process.

The main aim of this study is to optimize and retrofit the CTM process based on the downgrade of by-product steam. For this purpose, the influences of the reactor coolant temperature on the CTM process were considered from two aspects: (1) the overall process analyses, including the impact of the coolant temperature on the reactor and the overall process techno-economic performance; (2) the energy integration of the by-product steam in the reactor. The investigation reveals that the techno-economic performance of the CTM process is greatly improved when the coolant temperature is reduced to 187 °C because of the generation of low-pressure (LP) steam in the reactor.

CTM Process Description and Modeling

The flowsheet of an industrial CTM process is shown in Fig. 1. The CTM process consists of four units: COG preparation, reforming, methanol synthesis, and separation. In

the COG preparation unit, the sulfur in the COG (comprising organic and inorganic sulfur), which is harmful to the methanol synthesis catalyst, is removed by Fe–Mo hydrogenation and ZnO desulfurization processes. After that, the total sulfur in the COG is less than 0.1 ppm. In the reforming unit, most of the CH₄ in the COG is reformed to CO. Since this study focuses on the coolant temperature of the methanol synthesis reactor and the overall process performance, the flowsheet of the COG preparation and reforming units is not shown in this paper. Based on the data from the investigation of an industrial plant, the process was simulated using Aspen Plus software, which is a very useful simulation tool for chemical process design and optimization [30–32]. In the simulation model, COG feed and equipment operating parameters are set to be the same as those in industrial data. The Aspen “NRTL-RK” physical properties model is used in the simulation model.

Fig. 1 CTM process flowsheet

Reaction

This process employed medium-pressure (MP) methanol synthesis technology. Before reaction, the reformed COG feed, supplied from the upstream reforming unit, was compressed from 16.5 bar to 67.7 bar in a six-stage compression system (K1–K6). Each stage compressor has the same compression ratio following the common design heuristics. There is an intercooler between each two-stage compressor. For simplification, some intercoolers and compressors are omitted in Fig. 1. After compression, the gas was preheated to 213 °C by the reactor effluent in a feed-effluent heat exchanger.

This syngas was then fed into the tube side of the packed shell-and-tube reactor for methanol synthesis. The Aspen RPLUG reactor model with “counter-current thermal fluid temperature” heat-transfer option was employed for reaction simulation. The number of tubes and the length and diameter of the reactor are specified according to industrial data and remained unchanged in the subsequent optimization model. The total heat-transfer area is 1571 m². Cu/ZnO/Al₂O₃ catalyst was used in the reactor, and its specification is given in the model. The methanol synthesis reactor was conventionally cooled by MP boiling water (227 °C and 26.7 bar), and then, saturated MP steam (227 °C and 26.7 bar) was generated as a by-product. In the model, the inlet pressure and vapor fraction of the boiling water (coolant) were set as 26.7 bar and 0, respectively, and boiling water in the reactor was mainly used to maintain the appropriate temperature at the reactor bed by heat recovery. In the reactor, methanol synthesis reactions took place as Eqs. (1)–(3), and the

kinetics is in the form of water-shift reaction, as shown in Eqs. (2) and (3) [33].

The kinetics is depicted by Langmuir–Hinshelwood–Hougen–Watson (LHHW) type equations that are shown below. Equation (4) is the LHHW kinetic structure form, and Eqs. (5) and (6) are the reaction rate equations of reactions (2) and (3), respectively. The data used in the Aspen LHHW reaction model are given in detail in Table 1.

$$R = (\text{kinetic term}) \frac{(\text{driving force term})}{(\text{adsorption term})} \quad (4)$$

$$R_1 = (k_4 p_{\text{CO}_2} p_{\text{H}_2}) \frac{\left[1 - \frac{1}{K_{\text{E1}}} \left(\frac{p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}^3} \right) \right]}{\left[1 + k_3 p_{\text{H}_2\text{O}} / p_{\text{H}_2} + k_1 \sqrt{p_{\text{H}_2}} + k_2 p_{\text{H}_2\text{O}} \right]^3} \quad (5)$$

$$R_2 = (k_5 p_{\text{CO}_2}) \frac{\left[1 - \frac{1}{K_{\text{E2}}} \left(\frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}} \right) \right]}{\left[1 + k_3 p_{\text{H}_2\text{O}} / p_{\text{H}_2} + k_1 \sqrt{p_{\text{H}_2}} + k_2 p_{\text{H}_2\text{O}} \right]} \quad (6)$$

In addition to the methanol synthesis reactions, some side reactions also occurred as Eqs. (7) and (8). The Aspen RSTOIC reactor model is used for the side reactions with specific reaction conversions from the industrial data.

Table 1 Kinetic LHHW model parameters [33, 34]

$R_1: \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_4\text{O} + \text{H}_2\text{O}$			$R_2: \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	
Kinetic factor= $ke^{-E/RT}$	$k = 1.1 \times 10^{-3}$; $E = 36,688$ J/mol		$k = 1.2 \times 10^6$; $E = 94,743$ J/mol	
<i>Driving-force term expressions</i>				
Concentration exponents	Term 1	Term 2	Term 1	Term 2
CO/CO ₂	1	0	1	0
H ₂	1	−2	0	−1
CH ₃ OH/CO	0	1	0	1
H ₂ O	0	1	0	1
Coefficients	$A = 24.4, B = -7059.7, C = D = 0$		$A = -16.2, B = 4773.3, C = D = 0$	
<i>Adsorption term expression</i>				
Term exponent	3		1	
Concentration exponents	Term 1	Term 2	Term 1	Term 2
H ₂	0	−1	0	−1
H ₂ O	0	1	0	1
Adsorption constants	$A = B = C = D = 0$	$A = 8.2,$ $B = C = D = 0$	$A = B = C = D = 0$	$A = 8.2,$ $B = C = D = 0$

Pressure unit is N/m²; reaction rate unit is kmol/(kg_{cat} s); temperature unit is K

Separation and Columns

The reactor effluent was finally cooled to 43 °C and then fed into a gas–liquid separator (Sep) which was simulated with FLASH2 block model. Most of the gas separated from Sep was recycled to compressor K6 and then to the reactor for the unreacted reactants (H_2 , CO_2 , and CO) to be reused, and the remainder (Vent 1) was purged out as inert gas (CH_4 and N_2). The recycling/vent split ratio was set as 0.945 in an Aspen SPLIT block. The liquid separated from Sep was flashed at 4 bar to remove several light components (Vent 2). Hereafter, the crude methanol from flash tank was channeled to a distillation unit.

The crude methanol was pumped into a 40-stage pre-rectifying column (C1) on the 25th stage. The operation pressure of C1 was 1.6 bar. The condensation temperature was 68 °C, so cooling water was used in the condenser. After condensation, the remaining light components (Vent 3) were separated from the reflux drum. All the purged gases (Vent 1, Vent 2, and Vent 3) were fed into a combustion chamber and burned for heat recovery. The C1 reboiler heat duty was specified as 4.8 MW, in which LP steam was used. Afterwards, the liquid from the bottom of C1 was pumped into a pressurized-rectifying column (C2). The mass reflux ratio (RR) of C2 was specified as 2.5 in the model, and the top vapor was condensed by the bottom liquid of C3 in the economizer. The resulting heat duty of the reboiler using LP steam was 13.7 MW. Finally, the methanol-rich liquid from the bottom of C2 was directly sent into an atmospheric-rectifying column (C3), and its mass RR was specified as 2.3. All the columns were simulated with RADFRAC block model in Aspen Plus, and the detailed parameters and results of columns are shown in Fig. 1. The heat duty of the reboiler in C3 was specified as equal to that of the condenser in C2. The purity of the methanol product was specified as > 99.99 wt%. The methanol content of the bottom liquid was

specified as < 0.1 wt%. The above three specifications and column configuration are still applicable and unchanged in the subsequent optimization simulations.

Process Validation

To verify the reliability of the process model, the plant data (ID) and simulation results (SR) of the main streams are compared, as shown in Table 2. The relative error (RE) is below 6.3%, indicating that the simulation results are in good agreement with the plant data given in Fig. 1. Therefore, further analysis and optimization can be performed.

Methods

Per-Pass Conversion

In methanol synthesis, CO and CO_2 are product-forming reactants. The per-pass conversions of CO and CO_2 , which can show the utilization of reactants in the reactor, are expressed as Eqs. (9) and (10), respectively. The per-pass conversion of $\text{CO} + \text{CO}_2$ is expressed as Eq. (11).

$$x_{\text{CO}} = \frac{(f_{\text{CO}})_{\text{in}} - (f_{\text{CO}})_{\text{out}}}{(f_{\text{CO}})_{\text{in}}} \quad (9)$$

$$x_{\text{CO}_2} = \frac{(f_{\text{CO}_2})_{\text{in}} - (f_{\text{CO}_2})_{\text{out}}}{(f_{\text{CO}_2})_{\text{in}}} \quad (10)$$

$$x_{\text{CO}+\text{CO}_2} = \frac{(f_{\text{CO}_2} + f_{\text{CO}})_{\text{in}} - (f_{\text{CO}_2} + f_{\text{CO}})_{\text{out}}}{(f_{\text{CO}_2} + f_{\text{CO}})_{\text{in}}} \quad (11)$$

where x_{CO} , x_{CO_2} , and $x_{\text{CO}+\text{CO}_2}$ are the per-pass conversions of CO , CO_2 , and $\text{CO} + \text{CO}_2$, respectively, while $(f_{\text{CO}})_{\text{in}}$, $(f_{\text{CO}_2})_{\text{in}}$, $(f_{\text{CO}})_{\text{out}}$, and $(f_{\text{CO}_2})_{\text{out}}$ denote CO and CO_2 molar inflow and outflow rates of the reactor, respectively.

Table 2 Model validation

Composition	Recycling gas			Methanol 1			Methanol 2		
	ID (%)	SR (%)	RD (%)	ID (%)	SR (%)	RD (%)	ID (%)	SR (%)	RD (%)
H_2	76.52	76	−0.8						
CO	3.6	3.5	−2.8						
CO_2	4.0	3.8	−5						
N_2	14.66	15.5	5.7						
CH_4	0.64	0.6	−6.3						
CH_4O	0.58	0.6	3.4	0.9999	0.9999	0	0.9999	0.9999	0
Others				0.0001	0.0001	0	0.0001	0.0001	0
Flow rate (kmol h^{-1})	14,078	13,532	−3.9	447	446	−0.2	348	347	−0.3

Economic Evaluation

To optimize the industrial process, retrofitting is required, such as equipment replacement. Economic evaluation can well predict the retrofit investment needed for the optimization, as well as the energy cost and sales revenue. Equation (12) is used for economic evaluation. As the amount and composition of the reformed COG are fixed, no value needs to be assigned to the reformed COG. Table 3 shows the capital cost formulas of the heat exchanger and compressor [34–36]. The electricity cost was set as 0.1 \$/(kW h) [37]. The cost of LP steam (6 bar, 160 °C) used in heat exchanger 7(HX7) and the C1 and C2 reboilers was 7.8 \$/GJ. The sale price of methanol was set as 396.8 \$/t, deduced from the average price in 2014 [38]. The sale price of by-product steam was set as 6 \$/GJ. The vent stream contained mostly H₂ and CO, which can be burnt to recover its heat value. The fuel sale price was set as 6 \$/GJ [34].

$$\text{Income} = \sum (F_i \times P_i) - \sum (E_j \times C_j) - (\text{incremental capital})/3 \quad (12)$$

where F_i is the flow rate of methanol product, vent stream, and by-product steam, respectively; E_j is the energy consumption in electricity and LP steam, respectively; P and C are product price and energy cost, respectively.

Energy and Exergy Analyses

Energy efficiency is an important tool for evaluating a chemical process according to the first law of thermodynamics [39], which is calculated as

$$\eta_1 = \frac{\sum E_o}{\sum E_{in}} \times 100\% \quad (13)$$

where η_1 denotes energy efficiency and E_o and E_{in} are the total energy output and input based on low heat value (LHV), respectively.

Exergy efficiency offers a unique way to distinguish the energy to be used and detect the insufficiency of a process according to the second law of thermodynamics [40]. It is calculated as Eq. (14), where η_2 denotes exergy efficiency and EX_o and EX_{in} are the total exergy output and input, respectively. In the exergy efficiency calculation, the reference conditions, $T_0 = 298.13$ K and $P_0 = 1$ bar, are assumed [41].

$$\eta_2 = \frac{\sum EX_o}{\sum EX_{in}} \times 100\% \quad (14)$$

The material stream exergy can be calculated by Eqs. (15)–(17). The electricity exergy value is equal to the amount of electricity used, and the heat exergy is calculated by Eq. (18) [42].

$$EX = EX_{ch} + EX_{ph} \quad (15)$$

$$EX_{ch} = \sum x_i EX_{ch}^{0,i} + 8.314 T_0 \sum x_i \ln x_i \quad (16)$$

$$EX_{ph} = \sum x_i [(H - H_0) - T_0 (S - S_0)]_i \quad (17)$$

$$EX_{heat} = Q \left(1 - \frac{T_0}{T} \right) \quad (18)$$

where EX_{ch} , EX_{ph} , and $EX_{ch}^{0,i}$ are the chemical exergy, physical exergy, and the standard chemical molar exergy of component i , respectively; x_i is the molar fraction of component i ; H and S are the molar enthalpy and entropy under the working conditions, respectively; H_0 and S_0 denote the standard values of the molar enthalpy and entropy under the reference conditions, respectively; Q and T denote the amount of heat and the working temperature. The LHV and standard chemical molar exergy of different components involved are shown in Table 4 [22].

Table 3 Economic data

Item	Description
Heat exchanger	Capital cost = $7296 \times (\text{area})^{0.65}$ Area = (heat duty)/(heat transfer coefficient) (differential temperature)
Compressor	Capital cost = $1293 \times 517.3 \times 3.1 \times (\text{power})^{0.82}/280$
Energy cost	LP steam = 7.8 \$/GJ Electricity = 0.1 \$/(kW h)
Product price	Methanol = 396.8 \$/t By-product steam = 6 \$/GJ Vent stream = 6 \$/GJ
Payback period	3 Years

Table 4 LHV and the standard chemical molar exergy of different components

Component	LHV (kJ/mol)	Standard chemical exergy (kJ/mol)
H ₂	241.7	236.0
H ₂ O	–	9.5
N ₂	–	0.7
CO	283.1	275.1
CO ₂	–	19.9
CH ₄	803.7	831.2
CH ₄ O	638.5	718.0

Results and Discussion

As mentioned earlier, the coolant temperature of the methanol synthesis reactor is a critical factor which influences the methanol production and reactor thermal stability. In this section, the effects of different coolant temperatures on the process techno-economic performance are analyzed to find the optimal coolant temperature. To implement the optimal coolant temperature, other operating parameters need to be adjusted for suitability; therefore, other operating parameters are also explored and optimized in this section, including the inlet temperature of the reactor, recycling/vent split ratio, and column parameters. In addition, the energy integration of the by-product steam is also analyzed. During the process optimization simulation in Aspen Plus, some specifications are fixed. To reduce transformation in equipment, the configuration of all the columns and the reactor is fixed following the industrial plant configuration. The methanol product requirement is unchanged. In addition, the heat duty of C3 reboiler (QR3) is specified as equal to that of the C2 condenser (QC2). The minimum heat-transfer temperature difference in heat exchanger is set as 13 °C.

Analysis and Optimization of Coolant Temperature

Effects of Coolant Temperature on Reactor Performance

Since the methanol synthesis reaction is strongly exothermic, low temperatures would increase the chemical equilibrium constant and then promote methanol synthesis. But extremely low temperatures would limit reaction kinetics and then hinder methanol synthesis. These jointly determine the extent of methanol synthesis.

With the other parameters kept constant, the temperature inside the reactor and methanol mass fraction profiles along the reactor at different coolant temperatures are shown in

Fig. 2. The temperature inside the reactor increases with the coolant temperature (Fig. 2a), which suggests that low coolant temperatures are more favorable to the catalyst life and that the coolant absorbs more heat. In addition, the methanol mass fraction increases with the coolant temperature in the front section of the reactor (first 0–4 m along the reactor) but not in the back section (Fig. 2b). For the 227 °C coolant temperature, the methanol mass fraction is the highest in the front section, but becomes the lowest at the reactor outlet. Finally, a lower coolant temperature is more beneficial to the methanol synthesis. These suggest that the phenomenon occurring in the front section of the reactor is kinetically limited, while chemical equilibrium plays a leading role in the latter section. As a result, when the coolant temperature is 187 °C, the methanol mass fraction at the reactor outlet reaches its highest.

Effects of Coolant Temperature on the Overall Process Performance

The final goal is to achieve maximum income after the overall process. In this section, the effects of the coolant temperature on the technical and economic performance of the overall process are discussed and are depicted in Fig. 3. The per-pass conversions of CO, CO₂, and CO + CO₂ evidently change as the coolant temperature increases (Fig. 3a). The per-pass conversions of CO (0.789) and CO₂ (0.276) are maximum at coolant temperatures of 177 and 197 °C, respectively. The evidence of different temperatures suggests that the reactions of CO and CO₂ to methanol are differently sensitive to the coolant temperature. The maximum CO + CO₂ per-pass conversion (0.557) is reached at 187 °C, which corresponds with the methanol mass fraction profiles analysis in the previous section. Obviously, higher CO + CO₂ per-pass conversion means less unreacted gas, and consequently more methanol yield and less recycling and vent gas (Fig. 3b). At

Fig. 2 Effects of the coolant temperature on **a** the temperature inside the reactor and **b** methanol mass fraction along the reactor

Fig. 3 Effects of the coolant temperature on the technical and economic performances of the CTM process. **a** Per-pass conversion, **b** flowrate, **c** energy, **d** economic performance

187 °C, the recycling gas flow is the least, which reflects the least compressor power (Fig. 3c). However, QR2 and QC2/QR3 are maximum at 187 °C as more methanol yield indicates more feed to the columns. Afterwards, as the coolant temperature increases, the by-product steam energy recovered from the reactor decreases significantly. This energy could be integrated to the distillation column reboilers, so that the steam energy variation would influence the energy integration of the process.

In economic terms, Fig. 3d shows the total energy cost, capital investment, and income performance of the process while varying the coolant temperature. At 187 °C, the total energy cost is minimum, but in contrast, the capital investment is the highest. This is because at this temperature, the heat duties of the distillation column reboilers and condensers are greater than the conventional heat duties (at 227 °C), as shown in Fig. 3c, resulting in new heat exchanger investments. Even so, the highest income is reached at 187 °C.

In summary, if the coolant temperature is optimized to 187 °C, the CO + CO₂ per-pass conversion could be improved by 25%, and the recovered energy from the reactor could increase by 37.6%, saving energy and yielding economic benefits. Therefore, the coolant temperature is clearly very important for process optimization.

Analyses and Optimizations of Other Parameters

Reactor Inlet Temperature

In addition to the coolant temperature, the reactor inlet temperature is another important factor affecting the thermodynamic equilibrium. A high inlet temperature favors kinetics but tends to require large preheating duty. Therefore, in this section, the effects of the inlet temperature on the CO + CO₂ per-pass conversion and economics of the CTM process at different coolant temperatures are analyzed and illustrated in Fig. 4.

Higher inlet temperatures have positive effects on CO + CO₂ per-pass conversion at coolant temperatures of 167–207 °C (Fig. 4a), indicating that higher inlet temperatures or lower coolant temperatures are conducive to the methanol synthesis. When the coolant and inlet temperatures are 177 and 253 °C, respectively, the CO + CO₂ per-pass conversion is the highest; however, the process realizes the maximum income at the coolant temperature of 187 °C and inlet temperature 213 °C (Fig. 4b). This is due to the new capital investment and energy cost caused by higher syngas preheating duty required by the high inlet temperature. Actually, the capital investment, total energy cost, and income at different inlet and coolant

Fig. 4 Effects of the inlet temperature on **a** CO+CO₂ per-pass conversion and **b** income at different coolant temperatures

temperatures are calculated. For simplification, only the income is depicted in Fig. 4b. From the results, a coolant temperature of 187 °C and an inlet temperature of 213 °C are selected for the optimized process because of the corresponding maximum income.

Recycling/Vent Split Ratio

Figure 5 presents the effects of recycling/vent split ratio on the technical and economic performances of the CTM process at the optimal coolant temperature of 187 °C. The CO, CO₂, and CO+CO₂ per-pass conversions decrease as the split ratio increases (Fig. 5a). This suggests that the reaction kinetics is limited by the low reactant concentration during

Fig. 5 Effects of the recycling/vent split ratio on the technical and economic performance of the CTM process at coolant temperature of 187 °C. **a** Per-pass conversion, **b** flowrate, **c** energy, **d** economic performance

recycling. The recycling flow increases with the split ratio (Fig. 5b). At a split ratio of 0.945, the vent flow is minimum and the methanol yield is maximum. Furthermore, QR2 and QC2/QR3 are maximum at split ratio of 0.945–0.950 as more methanol yield reflects more feed to the columns; the power of compressor K6 increases with the split ratio (Fig. 5c). When the split ratio is higher than 0.945, the power is extremely high, which requires retrofitting the compression system and thus more capital investments (Fig. 5d). The lowest capital investment is attained at the split ratio of 0.945. The total energy cost decreases when the split ratio is lowered. In the split ratio range of 0.90–0.945, the income is relatively higher. Eventually, the split ratio of 0.945 is selected.

Operating Condition of the Distillation Columns

Through the coolant temperature optimization, the per-pass conversion has been significantly improved. This will inevitably change the distillation column feed composition and flow rate; thus, the operating conditions of the distillation

columns need to be adjusted. The reflux ratio (RR) of distillation column is an important variable that affects product purity and energy cost. As the distillation column sizes are fixed, the RR and feed stage location are selected as the optimization variables. C2 and C3 are the two most energy-consuming columns. For these columns, Figs. 6 and 7 show the effects of mass RR and feed stage location, respectively, on heat duty and product purity. By lowering the mass RR in the two columns, both the energy consumption and the methanol purity of the distillate are reduced (Fig. 6). Consequently, the mass RRs of C2 and C3 are set as 1.28 and 1.826, respectively, in the optimized process, which yields a methanol purity of 99.99 wt%.

By increasing the feed stage location of C2, the energy consumption is reduced and tends to be stable and the methanol purity is increased (Fig. 7a). When the feed stage location is greater than 38, the methanol product from C2 is qualified. By increasing the feed stage location of C3, the energy consumption first decreases and then increases, and the methanol purity first increases and then declines (Fig. 7b). When the feed stage location of C3 is between

Fig. 6 Effects of mass RR on the column heat duty and methanol purity of C2 (a) and C3 (b) at coolant temperature of 187 °C

Fig. 7 Effects of feed stage location on the column heat duty and methanol purity of C2 (a) and C3 (b) at coolant temperature of 187 °C

16 and 34, the methanol product from C3 is suitably pure. Consequently, the feed stage locations of C2 and C3 are set as 38 and 25, respectively.

Energy Integration of the Steam

So far, the optimization of process parameters is finished. Foremost, the coolant temperature is optimized to 187 °C. This means the 187 °C LP steam, instead of MP steam, is generated in the reactor shell side. As mentioned earlier, 160 °C LP steam is used in HX7 and C1 and C2 reboilers. This can be replaced by the 187 °C LP steam for heating in HX7 and the reboilers. The recovered heat by the LP steam is about 19.1 MW. The total required heat of HX7 and the reboilers is 15.4 MW, which can be sufficiently supplied by the LP steam. Therefore, in the optimized process, some by-product LP steam is integrated to column reboilers as a hot utility and some is routed for sale.

Figure 8 presents the energy and exergy balances of the optimized process. The total energy/exergy of the reformed COG was 213.2/213.9 MW, which was mixed with unreacted syngas (673.8/692.7 MW), and sent for methanol synthesis. Subsequently, the reactor effluent was sent to a separation unit and then a distillation unit, to yield methanol (144.7/162.7 MW). In addition, sufficient energy/exergy (19.1/6.7 MW) was recovered from the methanol synthesis unit in the form of steam. After the energy integration, 80.6% of the steam was for heat supply, and the rest 19.4% was sold as a by-product. The whole process suffered a total energy/exergy loss of about 32.7/18.3 MW. The total electrical energy consumption of the process was 9.1 MW.

Comprehensive Comparison of the Conventional and Optimized Process

Table 5 shows a detailed comparison of the conventional process and optimized process. Most importantly, unlike in the conventional process, the coolant temperature of the reactor in the optimized process was set as 187 °C instead of 227 °C; therefore, LP steam, instead of MP steam, was generated in the reactor. The mass RRs of C2 and C3 in the optimized process were adjusted as 1.280 and 1.826, respectively, and the other parameters were the same as those of the conventional process.

These transformations greatly improve the process. Because of the optimal coolant temperature, the reactor peak temperature is decreased by 32 °C, which is beneficial to the catalyst life, and the per-pass CO + CO₂ conversion of methanol synthesis reaction increases from 0.444 to 0.557. Accordingly, the recycling flow and vent flow decrease, which indicates less compressor work and fewer emissions, respectively, and the total methanol yield is increased by 3%. Furthermore, the by-product steam energy recovered from the reactor in the optimized process is 19.1 MW, which is 37.6% higher than that of the conventional process. Unlike in the conventional process, the by-product steam in the optimized process can supply enough heat to the whole process (15.4 MW), including reboilers and heater, and even has surplus (3.7 MW) for sale. Both the energy efficiency and exergy efficiency of the optimized process are increased to 66.8 and 73.5%, respectively. Consequently, the optimized process requires no capital investment and saves energy cost by 37.1%, increases income by 5.4 M\$/year, and reduces CO₂ emission by 21.3%.

Fig. 8 Energy and exergy balances of the optimized process at coolant temperature of 187 °C. **a** Energy flow and **b** exergy flow

Table 5 Comprehensive comparison of the conventional and optimized processes

Item	Conventional	Optimized
<i>Key parameters</i>		
Coolant temperature of reactor (°C)	227	187
Inlet temperature of reactor (°C)	213	213
Recycling/vent split ratio	0.945	0.945
C2 mass RR	2.500	1.280
C3 mass RR	2.300	1.826
<i>Technical performance</i>		
Per-pass conversion of CO	0.586	0.778
Per-pass conversion of CO ₂	0.236	0.275
Per-pass conversion of CO + CO ₂	0.444	0.557 (25%↑)
The reactor peak temperature (°C)	273	241
Methanol yield (kg/h)	25,382	26,141 (3%↑)
Vent flow (kmol/h) ^a	866	789
Recycling flow (kmol/h)	13,532	12,252
<i>Energy performance</i>		
Compressor K6 (MW)	4.8	4.5 (7.5%↓)
QR1 (MW)	4.8	4.8
HX7 (MW)	1.3	1.3
QR2 (MW)	13.7	9.2 (32.4%↓)
Reactor heat recovery (MW)	13.9	19.1 (37.6%↑)
By-product steam	MP steam (26.7 bar, 227 °C)	LP steam (11.7 bar, 187 °C)
Total electricity (MW)	9.5	9.1
Total steam consumption (MW)	19.7	15.4 (22.2%↓)
External steam (MW)	5.9	−3.7 ^b
Energy efficiency (%)	61.5	66.8
Exergy efficiency (%)	70.1	73.5
<i>Economic and environmental performance</i>		
Energy cost (M\$/year)	12.8	8.0 (37.1%↓)
Incremental income (M\$/year)	—	5.4
Incremental capital investment (\$)	—	0
Total CO ₂ emission ^c (kmol/h)	125.2	101.5
CO ₂ emission ^d (kmol/t-methanol)	4.9	3.9 (21.3%↓)

^aVent flow includes Vent 1, Vent 2, and Vent 3^bThe surplus steam for sale^cThe total CO₂ emission comes from the tail gas after full combustion of vent^dThe CO₂ emission is calculated from the total CO₂ emission divided by the methanol yield

Conclusion

In this paper, the effects of the reactor coolant temperature, as well as the key process parameters, on the techno-economic performance and energy integration of an industrial CTM process have been explored. The results suggest that the CTM process can be greatly improved and optimized when the coolant temperature is reduced to 187 °C, though

the by-product steam is downgraded to LP steam. Compared with the conventional process, the optimized process presents significant improvements as follows:

- (1) In the methanol synthesis reactor, the CO + CO₂ per-pass conversion is increased by 25%, and the total methanol yield is increased by 3%.
- (2) The energy, recovered from the reactor in the form of steam, is increased by 37.6%. After the energy integration, 80.6% of the steam is used to supply heat to the whole process, and the rest is routed for sale. As a result, the external steam consumption reduces from 5.9 MW to zero, and the energy and exergy efficiencies of the process are increased by 4–9%.
- (3) The optimized process requires no incremental capital investment and saves energy cost by 37.1%, increases income by 5.4 M\$/year, and reduces CO₂ emission by 21.3%.

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References

1. Chen WH, Hsu CL, Du SW (2015) Thermodynamic analysis of the partial oxidation of coke oven gas for indirect reduction of iron oxides in a blast furnace. *Energy* 86:758–771
2. Bermúdez JM, Arenillas A, Luque R et al (2013) An overview of novel technologies to valorise coke oven gas surplus. *Fuel Process Technol* 110:150–159
3. IEA (2007) Tracking industrial energy efficiency and CO₂ emissions. *Energy Policy* 30(10):849–863
4. National Bureau of Statistics of China (2016) Coke statistics reports for China. <http://data.stats.gov.cn/search.html>. Accessed 20 Apr 2018
5. Yang Z, Zhang Y, Wang X et al (2014) Design of two-stage membrane reactor for the conversion of coke-oven gas to H₂ and CO. *J Energy Chem* 23(4):411–413
6. Zhang X, Yang K, Liu Y et al (2010) Development and progress of efficient utilization technology of coke oven gas. *Chem Ind Eng Prog* 29(S1):322–324 (in Chinese)
7. Zhou L, Liu K, Sha Y (2013) Analysis of coke oven gas injection into BF then generate electricity. *Energy Metall Ind* 32(3):41–45 (in Chinese)
8. Wang S, Wang G, Jiang F et al (2010) Chemical looping combustion of coke oven gas by using Fe₂O₃/CuO with MgAl₂O₄ as oxygen carrier. *Energy Environ Sci* 3(9):1353–1360
9. Xie H, Yu Q, Zhang Y et al (2017) New process for hydrogen production from raw coke oven gas via sorption-enhanced steam reforming: thermodynamic analysis. *Int J Hydrog Energy* 42(5):2914–2923
10. Yi Q, Wu G, Gong M et al (2017) A feasibility study for CO₂ recycle assistance with coke oven gas to synthetic natural gas. *Appl Energy* 193:149–161

11. Dan X, Yan L, Yang Y (2014) Simulation and analysis of coke oven gas methanation process based on Aspen Plus. *Technol Dev Chem Ind* 43(5):52–57 (in Chinese)
12. Xiang D, Yang S, Mai Z et al (2015) Comparative study of coal, natural gas, and coke-oven gas based methanol to olefins processes in China. *Comput Chem Eng* 83:176–185
13. Man Y, Yang S, Xiao H et al (2015) Modeling, simulation and analysis for coal and coke-oven gas to synthetic natural gas. *CIESC J* 66(12):4941–4947 (in Chinese)
14. Xie H, Zhang J, Yu Q et al (2016) Study on steam reforming of tar in hot coke oven gas for hydrogen production. *Energy Fuels* 30(3):2336–2344
15. Li Z, Liu P, He F et al (2011) Simulation and exergoeconomic analysis of a dual-gas sourced polygeneration process with integrated methanol/DME/DMC catalytic synthesis. *Comput Chem Eng* 35(9):1857–1862
16. Man Y, Yang S, Zhang J et al (2014) Conceptual design of coke-oven gas assisted coal to olefins process for high energy efficiency and low CO₂ emission. *Appl Energy* 133:197–205
17. Bermúdez JM, Ferrera-Lorenzo N, Luque S et al (2013) New process for producing methanol from coke oven gas by means of CO₂ reforming. Comparison with conventional process. *Fuel Process Technol* 115:215–221
18. Razzaq R, Li C, Zhang S (2013) Coke oven gas: availability, properties, purification, and utilization in China. *Fuel* 113:287–299
19. Wang T (2005) Coke oven gas: technical and economic comparison of different utilization methods of power generation, hydrogen production, methanol production and direct reduced iron. In: Coal processing and utilization technology, market and industrialization information exchange conference and development strategy seminar in China. Xi'an, China, pp 241–243 (in Chinese)
20. Yi Q, Wu Y, Fan Y et al (2014) Economic evaluation of industrial chain extension solutions for coke oven gas to methanol and chemicals. *CIESC J* 65(3):1003–1011 (in Chinese)
21. Qian Y, Man Y, Peng L et al (2015) Integrated process of coke-oven gas tri-reforming and coal gasification to methanol with high carbon utilization and energy efficiency. *Ind Eng Chem Res* 54:2519–2525
22. Yi Q, Gong MH, Huang Y et al (2016) Process development of coke oven gas to methanol integrated with CO₂ recycle for satisfactory techno-economic performance. *Energy* 112:618–628
23. Gong M, Yi Q, Huang Y et al (2012) Coke oven gas to methanol process integrated with CO₂ recycle for high energy efficiency, economic benefits and low emissions. *Energy Convers Manag* 133:318–331
24. Wu Z, Li H, Wang W (2012) Process parameter optimization of COG reforming for a 300 kt/a methanol plant. *Nat Gas Chem Ind* 37(5):32–35 (in Chinese)
25. Manenti F, Cieri S, Restelli M (2011) Considerations on the steady-state modeling of methanol synthesis fixed-bed reactor. *Chem Eng Sci* 66(2):152–162
26. Shahrokhi M, Baghmisheh GR (2005) Modeling, simulation and control of a methanol synthesis fixed-bed reactor. *Chem Eng Sci* 60(15):4275–4286
27. Manenti F, Leon-Garzon AR, Bozzano G (2013) Energy-process integration of the gas-cooled/water-cooled fixed-bed reactor network for methanol synthesis. *Chem Eng Trans* 35:1243–1248
28. Manenti F, Leon-Garzon AR, Ravaghi-Ardebili Z et al (2014) Systematic staging design applied to the fixed-bed reactor series for methanol and one-step methanol/dimethyl ether synthesis. *Appl Therm Eng* 70(2):1228–1237
29. Bozzano G, Manenti F (2016) Efficient methanol synthesis: perspectives, technologies and optimization strategies. *Prog Energy Combust Sci* 56:71–105
30. König DH, Baucks N, Dietrich RU et al (2015) Simulation and evaluation of a process concept for the generation of synthetic fuel from CO₂ and H₂. *Energy* 91:833–841
31. Meng WX, Banerjee S, Zhang X et al (2015) Process simulation of multi-stage chemical-looping combustion using Aspen Plus. *Energy* 90:1869–1877
32. Khojasteh SY, Adams TA (2015) Integrated petroleum coke and natural gas polygeneration process with zero carbon emissions. *Energy* 91:479–490
33. Bussche KMV, Froment GF (1996) A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst. *J Catal* 10(156):1–10
34. Luyben WL (2010) Design and control of a methanol reactor/column process. *Ind Eng Chem Res* 49(13):6150–6163
35. Douglas JM (1988) Conceptual design of chemical processes. McGraw-Hill, New York
36. Turton R, Bailie RC, Whiting WB et al (2012) Analysis, synthesis, and design of chemical processes, 4th edn. Prentice-Hall, Englewood Cliffs
37. Man Y, Yang S, Qian Y (2016) Integrated process for synthetic natural gas production from coal and coke-oven gas with high energy efficiency and low emission. *Energy Convers Manag* 117:162–170
38. Xiang D, Yang S, Liu X et al (2014) Techno-economic performance of the coal-to-olefins process with CCS. *Chem Eng J* 240:45–54
39. Ranjan KR, Kaushik SC (2013) Energy, exergy and thermo-economic analysis of solar distillation systems: a review. *Renew Sustain Energy Rev* 27:709–723
40. Gökgedik H, Yürüsoy M, Keçebaş A (2016) Improvement potential of a real geothermal power plant using advanced exergy analysis. *Energy* 112:254–263
41. De Jong ED, Keuken H, Van Der PE et al (1996) Exergy analysis of industrial processes using AI techniques. *Comput Chem Eng* 20(96):1631–1636
42. Xiang D, Xiang J, Sun Z et al (2017) The integrated coke-oven gas and pulverized coke gasification for methanol production with highly efficient hydrogen utilization. *Energy* 140:78–91