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Conceptual Design and Techno-Economic Analysis of a Novel Coal-based Polygeneration Process of MCFC and Methane Synthesis with a Waste Heat Recovery System

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This work aims to develop and techno-economically analyze a novel coal-based polygeneration process of Molten Carbonate Fuel Cell (MCFC) and methane synthesis with a waste heat recovery system. In this process, the unshifted syngas without entering Rectisol is directly mixed with a part of H_2-rich syngas to reduce the energy consumption of Rectisol and flexibly adjust the H/C ratio. An extended Duran-Grossmann (D-G) model for waste heat recovery steam cycle optimization is proposed by conducting Heat Integration among the whole process. According to techno-economic analysis, the annual capital cost of the proposed system is 50,006,000 $, the overall exergy efficiency is 56.3 %. Compared with the base plant, the MCFC with power generation of 16.98 MW is applied instead of the Rankine cycle (RC), which results in a 14 % increase in the efficiency of the power generation system. The major contributions derived from this work are of significant aid in highlighting strong potentials for overall performance enhancement via polygeneration optimization.

1. Introduction

Coal, as the dominant resource, is widely used to produce chemicals and power, which is an effective way to improve energy efficiency and process economy. However, there exists overcapacity in the single coal-based process. In order to realize the diversification and the high value of product, chemicals-electricity polygeneration system has been proposed and proven as a significant process. A growing number of researchers are devoted to investigating more advanced clean energy technologies integrated with multi-product polygeneration process, which facilitates improving the market competitiveness and adaptability.

The demand for natural gas is increasing with an annual rate of 18 %, whose external dependence is up to 43 % in China. Recently, several studies focused on the coal-to-synthetic natural gas (SNG) integrated with other processes. Man et al. (2016) proposed a co-feed of coal and coke-oven gas into SNG process to decrease CO_2 emissions. Li et al. (2016) proposed a polygeneration system of SNG and power production with better energy and environmental performances.

The fuel cell (Ozkan G et al. 2016), as an alternative for the existing inefficient power technologies, directly transforms the chemical energy to the electrical energy. In addition, it is a clean energy technology since only water is produced when H_2 reacts with O_2. Molten Carbonate Fuel Cell (MCFC) is identified as the most suitable technology due to its high efficiency, low on-site emissions, high poisoning tolerance, excellent durability and compatibility with other processes. To this end, numerous polygeneration processes with MCFC have been proposed. Jienkulsawad et al. (2015) introduced various configurations of the integrated Solid Oxide Fuel Cell - MCFC system to determine a suitable design of the integrated fuel cell system. Duan et al. (2016) developed a coal-fired power plant with CO_2 capture by integrating MCFC, which had an obvious heat performance advantage compared with the conventional CO_2 capture method. Hosseini et al. (2019) proposed a hybrid MCFC-methanol synthesis process-combined power cycle system, in which exergetic performance assessment was conducted to show the outstanding overall efficiency enhancement.

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With the mentioned concern, the polygeneration processes, such as coal-to-SNG coupled with conventional power generation systems have been proved as an effective technology. Due to low efficiency of conventional power generation systems which convert chemical energy to mechanical energy and then to electrical energy, fuel cells are an effective alternative, but rarely being investigated to integrate fuel cell with coal-based processes. In this paper, coal is used as feedstock to integrate coal-to-SNG with MCFC. In addition, techno-economic analysis is conducted to demonstrate the superiority of the proposed system.

2. Conceptual design for a polygeneration process of MCFC and methane synthesis

As discussed in the Introduction section, the proposed system is shown in Figure 1.

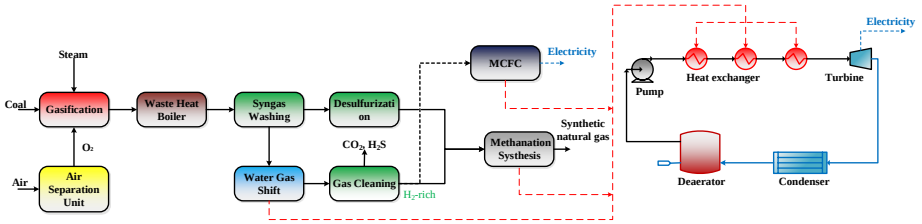


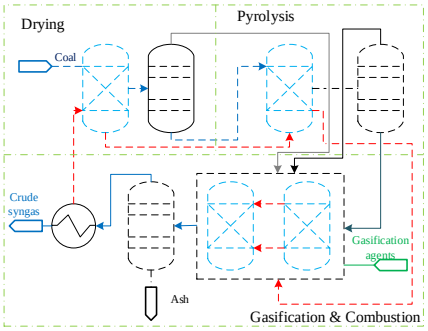
Figure 1: Schematic diagram of the proposed system

The whole process is mainly composed of gasification unit (GAS), water gas shift unit (WGS), Rectisol unit, methanation unit and MCFC. In the proposed system, coal is converted to crude syngas, which is then divided into two parts after heat recovery and washing. One part goes into WGS where crude syngas is converted to H_2-rich syngas, and then enters the Rectisol unit. In order to maximize the CO_2 mole fraction, another unshifted syngas directly enters the Sulfur removal unit without entering the Rectisol unit. Compared with the conventional process, since unshifted syngas is not mixed with H_2-rich syngas, H_2-rich syngas in the Rectisol unit has the largest CO_2 molar fraction, causing lower energy consumption. Finally, a part of H_2-rich gas is mixed with the unshifted syngas to satisfy the H/C requirements of methanation unit, while the other part of H_2-rich gas is fed into MCFC. In addition, a branch waste heat recovery steam cycle (WHRSC) at three pressure levels is proposed to conduct global waste heat recovery based on an extended D-G model (Duran M.A. et al. 1986).

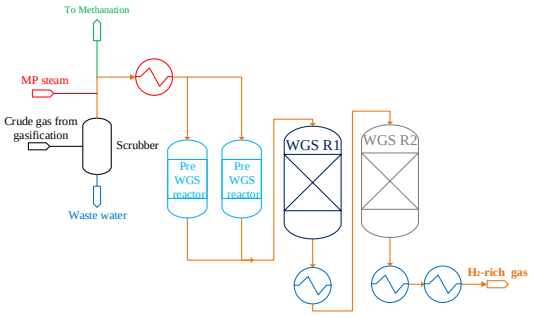
3. Process model

3.1 GAS and WGS model

As shown in Figure 2a, the gasifier is constructed and divided into four zones to be simulated in Aspen Plus: drying, pyrolysis, gasification and combustion. The gasification temperature in the gasifier ranges from 1,400 °C to1,600 °C. Drying and Pyrolysis occur at the top of the gasifier, generating tar and gas products. In the gasification and combustion zone, the pyrolysis products react with the gasification agent to form crude syngas, ash and unreacted carbon. The property method RK-SOAVE is selected. General coal enthalpy model (HCOALGEN) and general coal density model (DCOALGEN) are adopted as the enthalpy model and density model of the unconventional components.



(a)



(b)

Figure 2: Simulation flow sheet for (a) GAS and (b) WGS

As shown in Figure 2b, the crude syngas out of GAS enters the scrubber firstly where the tar and ash are washed out. After pre-treatment, syngas enters the two-stage adiabatic reactors in which WGS reaction occurs, as shown in Eq(1). Since the reaction is a strongly exothermic process, the syngas exiting the high-temperature reactor needs to be cooled to proper temperature, and then enters the low-temperature reactor. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) model is used, as expressed by Eq(2) and Eq(3).

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41 \text{ kJ/mol} \tag{1}$$

$$r_{WGS} = k_{WGS} \exp\left(-\frac{E_{WGS}}{RT}\right)\left(p_{CO}p_{H_2O} - p_{H_2}p_{CO_2} / K_{WGS}\right) \tag{2}$$

$$\ln\left(K_{WGS}\right) = -13.148 + \frac{5693.5}{T} + 1.077\ln T + 5.44\times10^{-4}T \tag{3}$$

where K_{WGS} is equilibrium constant, k_{WGS} is kinetic factor, set as 1.612×10^{-5} kmol/(s·m^3·Pa^2), E_{WGS} is activation energy, set as 47,400 J/mol.

3.2 Methanation unit

Five-stage methanation process over Ni-based catalyst is adopted to produce synthetic natural gas. The corresponding operating temperature ranges from 250 °C to 700 °C. The first two reactors are the main methanation reactors where most syngas is converted to methane, while the rest small amount of syngas reacts in the remaining three reactors. The CO hydrogenation, CO_2 hydrogenation and WGS occur simultaneously, expressed by Eqs(4) - (6).

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_{298K} = -206 \text{ kJ/mol} \tag{4}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298K} = -164.53 \text{ kJ/mol} \tag{5}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298K} = -41.47 \text{ kJ/mol} \tag{6}$$

The reactions of CO hydrogenation and WGS are selected as the independent reactions for modeling methanation. Expressions of the LHHW type kinetic equation are shown by Eqs(7) - (9).

$$r_{METH} = \frac{k_{METH}}{p_{H_2}^{2.5}} \cdot \frac{(p_{CH_4}p_{H_2O} - p_{H_2}^3 p_{CO_2} / K_{METH})}{\text{DEN}^2} \tag{7}$$

$$r_{WGS} = \frac{k_{WGS}}{p_{H_2}} \cdot \frac{(p_{CO}p_{H_2O} - p_{H_2}p_{CO_2} / K_{WGS})}{\text{DEN}^2} \tag{8}$$

$$\text{DEN} = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O}/p_{H_2} \tag{9}$$

Where K_m, k_m, K_n and p_n are equilibrium constant, kinetic rate constant of reaction m (m = 1, 2), adsorption constant and partial pressure of species n (n= CH_4, CO, CO_2, H_2, and H_2O).

3.3 MCFC model

The MCFC model is built to calculate voltage and current and estimate the electrochemical performance. The corresponding structure diagram and simulation process of MCFC are shown in Figure 3a and Figure 3b. The reaction that occurs in the MCFC is presented in Eqs(10) - (11).

Cathode reaction: $$O_2 + 2CO_2 + 4e^- = 2CO_3^{2-} \tag{10}$$

Anode reaction: $$H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^- \tag{11}$$

In the anode-side, H_2 reacts with CO_3^{2-} to produce carbon dioxide, water and electron. The rest of unreacted fuel is sent to after-burner, while the electrons reach the cathode from the external circuit. At the cathode-side, O_2 reacts with electron and CO_2 from the after-burner to yield CO_3^{2-}. Then, CO_3^{2-} is transferred to the anode-side through the electrolyte. The electricity is produced by passing the electrons through an external circuit. The Nernst equation is applied to calculate the ideal reversible voltage of MCFC and the corresponding output power of MCFC is shown below.

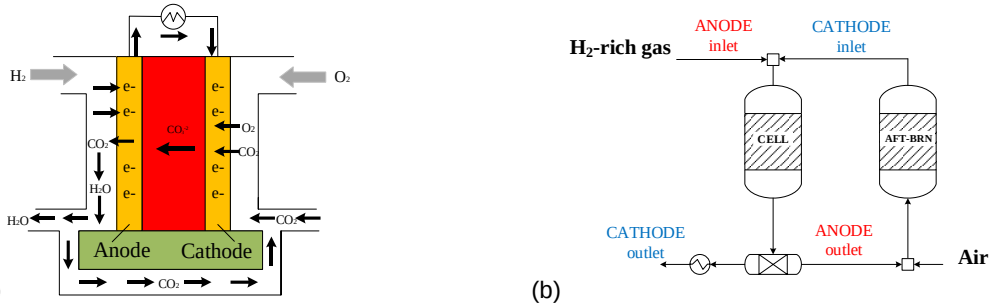


Figure 3: (a) The structure diagram of MCFC and (b) The simulation process of MCFC

$$V = \frac{\Delta G}{nF} + \frac{R_g(T\text{-}273.5)}{nF}\ln[\frac{P_{H_2,an}\left(P_{O_2,an}\right)^{0.5}P_{CO_2,ca}}{P_{H_2O,an}P_{CO_2,an}}]\text{-}i(R_{an}+R_{ca}+R_{ohm}) \tag{12}$$

$$W = \xi \cdot V \cdot i \cdot A \tag{13}$$

Where V is the real voltage (V), ΔG is the change in Gibbs free energy (kJ/kmol), n is the molar number of electrons released in regard with dissociation of H_2, F is the Faraday constant (96,485.3329 A·s·mol^{-1}), R_g is the universal gas constant (8.314 J/(mol·K)), T is the operating temperature of MCFC (°C), P_i is the partial pressure (atm) of component. i is the current density (A/m^2) and R is the polarization losses (Ωm^2). The polarization losses consist of activation (anode), ohmic (electrolyte) and concentration (cathode) losses, as shown below.

$$R_{an} = 2.27\times10^{-9}\times\exp\left(\frac{E_{act,an}}{RT}\right)P_{H_2}^{-0.43}P_{CO_2}^{-0.17}P_{H_2O}^{-10} \tag{14}$$

$$R_{ca} = 7.505\times10^{-10}\times\exp\left(\frac{E_{act,ca}}{RT}\right)P_{O_2}^{-0.43}P_{CO_2}^{-0.09} \tag{15}$$

$$R_{ohm} = 0.5\times10^{-4}\times\exp\left[3016\left(\frac{1}{T}-\frac{1}{923}\right)\right] \tag{16}$$

Table 1: The operating conditions of MCFC.

Parameter	Unit	Value	Parameter	Unit	Value
Mean temperature	°C	650	Cell area	m^2	0.7
Pressure	kPa	101	Current density	A/m^2	1,500
Number of cells	-	21,872	Fuel utilization	%	85

4. WHRSC and Heat Integration model (Duran M.A. et al. 1986)

In this section, WHRSC is proposed to recover waste heat from the WGS, MCFC and methanation units, as shown in Figure 4. The steam at three pressure levels are yielded in different superheaters and then sent to the steam turbines to generate electrical power. In order to achieve Heat Integration and waste heat recovery with steam optimization, an extended D-G model is proposed. In this model, the flowrates of different grade steams in the WHRSC are optimized under the fixed process stream parameters, aiming at the maximum power generation. The Heat Integration model of the process is a threshold problem which only requires cold utility (Q_C). Hot utility (Q_H) is set to be zero. The corresponding constraints are shown in Eqs(17) to (20).

$$\begin{aligned} Z_H^P(x) = &\sum_{j\in C} f_j c_j\left[\max\left\{0, t_j^{out}-\left(T^P-\Delta T_m\right)\right\}-\max\left\{0, t_j^{in}-\left(T^P-\Delta T_m\right)\right\}\right] \\ &-\sum_{i\in H} F_i C_i\left[\max\left\{0, T_i^{in}-T^P\right\}-\max\left\{0, T_i^{out}-T^P\right\}\right] \end{aligned} \tag{17}$$

$$\Omega(x) = \sum_{i\in H} F_i C_i\left(T_i^{in}-T_i^{out}\right)-\sum_{j\in C} f_j c_j\left(t_j^{out}-t_j^{in}\right) \tag{18}$$

$$Z_H^P(x) \le Q_H \tag{19}$$

$$\Omega(x)+Q_H-Q_C=0 \tag{20}$$

Where $Z_H^P(x)$ is heat deficit, f_j, c_j, t_j^{out} *and* t_j^{in} are flow rates, heat capacity, outlet temperature and inlet temperature of cold stream. F_i, C_i, T_i^{out} and T_i^{in} are flowrates, heat capacity, outlet temperature and inlet temperature of hot stream. $\Omega(x)$ is the difference of heat content between hot and cold process streams, T^P is the candidate Pinch Point, ΔT_m is the temperature difference.

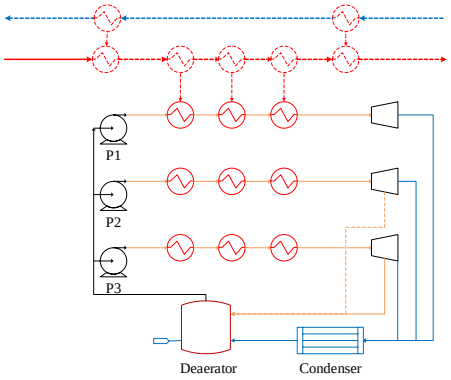


Figure 4: Simulation flowsheet of WHRSC

5. Techno-economic analysis

Exergy is made up of chemical exergy and physical exergy. The physical exergy is determined by the enthalpy and entropy of streams, and chemical exergy is calculated by the mole fraction and standard chemical exergy of each component, as shown in Eqs(21) - (23). The lignite exergy is calculated by empirical formula, as shown in Eq(24). Economic performance is analyzed to show the effectiveness of the proposed process. The annual capital cost (ACC) is estimated by Eqs(25) - (27).

$$Ex = Ex^{ch} + Ex^{ph} \tag{21}$$

$$Ex^{ch} = \sum_{j=1}^{n} b_{ch,j} \cdot x_{ij} \tag{22}$$

$$Ex^{ph} = (H - T_0 S) - (H_0 - T_0 S_0) \tag{23}$$

$$Ex_{coal} = m_{coal} \times Q_{net} \times \left(1.0064 + 0.1509 \times \frac{\omega(H)}{\omega(C)} + 0.0616 \times \frac{\omega(O)}{\omega(C)} + 0.0429 \times \frac{\omega(N)}{\omega(C)}\right) \tag{24}$$

$$I_2 = I_1 \left(\frac{\delta_2}{\delta_1}\right)^{sf} \tag{25}$$

$$TCI = I_2(1+\sum RF_i) \tag{26}$$

$$ACC = TCI(\gamma(1+\gamma)^n) / ((1+\gamma)^n - 1) \tag{27}$$

Where *Ex* is exergy, *H* is enthalpy, *S* is entropy, $b_{ch,j}$ is the standard chemical exergy, *I* and δ are the equipment investment and the production scale, *sf* is index factor, *TCI* is the total capital investment, *RF* denotes the ratio factor, γ is the interest rate and *n* denotes the plant life time.

6. Results and discussions

A base plant with the same operating conditions is simulated, the only difference between the base plant and the proposed system is that RC is applied to generate power instead of MCFC. The overall performance specifications of the base plant and the proposed system are shown in Table 2.

According to techno-economic analysis, the ACC of the proposed system is 50,006,000 $. The overall exergy efficiency is 56.3 %, which recognizes the exergy efficiency enhancement and economy improvement attributable to the material and energy sharing. In the base plant, H_2-rich gas is burned to release chemical

energy and generate 13.30 kW of power through RC. In the proposed system, the MCFC with power generation of 16.98 MW is applied, which results in a 14 % increase in the efficiency of the power generation system.
From the table we can also see the proposed system is successfully capable of producing 360 kmol/h of medium pressure (MP) steam and 434 kmol/h of SNG. In the conventional coal-to-SNG, all the waste heat is used to generate MP steam, while in this paper, WHRSC is proposed and optimized based on the extended D-G model, which greatly enhances the heat recovery. All the steam produced by WHRSC is fed into turbine to generate electricity, producing 20.99 MW electrical power. In Rectisol, CO_2 molar fraction decides CO_2 capture energy consumption. High CO_2 molar fration can decrease energy consumption effectively. In this process, a part of crude syngas is directly seperated to downstream to adjust H/C, so that almost all CO is converted in WGS, leading to high CO_2 molar concentration.

Table 2: Overall performance specifications of the base plant and the proposed system

Inputs			Products in the base plant			Products in the proposed system		
Unit	Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value
	Lignite/kg/h	30,000	GAS	MP/kmol/h	360	GAS	MP/kmol/h	360
GAS	Steam/kg/h	6,200	RC	Power/MW	13.30	MCFC	Power/MW	16.98
	Oxygen/kg/h	9,900					Voltage/V	0.75
WGS	Steam/kmol/h	212	Methanation	SNG/kmol/h	434	Methanation	SNG/kmol/h	434
MCFC	Syngas/kmol/h	624		Purity/%	92		Purity/%	92
Methanation	Syngas/kmol/h	1,317	WHRSC	Power/ MW	20.99	WHRSC	Power/MW	20.99

7. Conclusion

In this work, a novel coal-based polygeneration process of methane synthesis and MCFC is proposed to realize sustainable and eco-benign using of coal resources. In the proposed system, coal is converted to syngas and then partly shifted to H_2-rich gas. Unshifted syngas without entering Rectisol is directly mixed with a part of H_2-rich syngas and then sent to methanation, which results in lower Rectisol energy consumption. The other part H_2-rich gas is fed to MCFC, producing 16.98 MW electrical power. In addition, WHRSC produces 20.99 MW electrical power by conducting heat recovery from WGS, MCFC and methanation based on the extended D-G model. According to techno-economic analysis, the ACC of the proposed system is 50,006,000 $ and the overall exergy efficiency is 56.3 %. Compared with the base plant, the MCFC with power generation of 16.98 MW is applied instead of RC, which results in a 14 % increase in the efficiency of the power generation system. The proposed system integrates the traditional coal-to-SNG with the novel MCFC successfully.

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