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Optimization of Syngas Production Systems Subject to Almost Net-zero CO_2 Emission *

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***Abstract*—This work describes two different configurations of syngas production processes using a combination of steam methane reforming (SMR) and dry reforming of methane (DRM). The ideal SMR+DRM process ensures the maximum product yield, the heat-integrated SMR+DRM process fulfills the maximum heat recovery, and the stand-alone SMR+DRM process effectively suppress net CO_2 emissions. Through kinetic modeling and specific optimization algorithms, the syngas production systems subject to almost net-zero CO_2 emissions are successfully verified by simulations in Aspen Plus environment.**

I. INTRODUCTION

The efficient syngas production (a mixture of H_2 and CO) is gaining significant attention since it can be used to produce a variety of liquid fuels such as methanol, ethanol, and dimethyl ether (DME) through the Fischer-Tropsch process. The SMR is a catalytic and energy efficient technology for producing a H_2-rich syngas [1], but the steam reforming is an endothermic reaction in which the operating temperature is usually over 800K. The DRM is a potential method in production of CO-rich syngas by consuming greenhouse gases such as CH_4 and CO_2. This process is attractive from the environmental and economic viewpoint because of the potential utilization of greenhouse gases as resources. Similarly, the main obstacle with respect to the commercialization of the DRM process is given by the severe catalyst deactivation due to carbon deposition. The highly active catalysts with superior lifetime stability in the DRM have been studied with experimental tests and kinetic analysis [2-4]. The DRM process is not conducive to producing hydrogen since the hydrogen may react with the reactant CO_2 to produce water at specific operating conditions [5]. Through thermodynamic equilibrium analysis of all possible reactions in the DRM, carbon formation as well as water production can be improved by specific ratios of CO_2:CH_4:O_2 and modified catalysts at higher operating temperature [6, 9]].

The SMR is the best option for hydrogen production due to its relatively low cost, but the issues of energy-saving and carbon dioxide reduction have recently been attracting much attention. The heat integration design using heat exchanger network and pinch analysis can be applied to maximize the heat recovery and identify thermal efficiency limit of the SMR process [8-10]. To address the benefits of the combination of different reforming reactions, Supat et al. [11] showed that a combination of noncatalytic partial oxidation and steam reforming has a benefit in terms of balancing the heat load. However, a typical steam reforming with oxygen reactor operated at about 2200 K in the combustion zone and 1200-1400 K in the catalytic zone. Song and Pan [12] proposed a novel process with catalytic tri-reforming of methane (SMR, POM and DRM) to achieve high CH_4 conversion and high CO_2 conversion for producing syngas over supported nickel catalysts at 800-850 °C. Halmann and Steinfeld [13] considered flue gases from coal, gas, or oil-fired power stations as reactants of tri-reforming of methane to achieve fuel saving and CO_2 emission avoidance. For tri-reforming reactions, the specific catalyst composition and preparation method strongly affect CO_2 and CH_4 conversion. Recently, Zhou et al. [14] showed that the high temperature (over 1173K) could significantly promote the multi-reforming process while avoiding the problem of catalyst deactivation.

To develop a new process from laboratory scale to industrial scale, the process design, optimization and simulation are critical procedures. Currently, the kinetic models of tri-reforming reactions are incomplete, and the high-activity and durable reforming catalysts are quite rare. In light of kinetic models of DRM and SMR which have been verified by experiments and thermodynamic equilibrium analysis, Gangadharan et al. [15] showed that a combination of SMR and DRM (SMR+DRM) was competitive with the popular SMR. The utility costs and energy consumption of the SMR+DRM process is higher than the SMR process, but this process can effectively reduce carbon emissions. Based on optimal operating conditions, Lim et al. [16] showed that a SMR+DRM process could reduce net CO_2 emission by 67%. However, these SMR+DRM processes needs to consume a large amount of external energy to keep the high CO_2 conversion.

In this article, we propose new syngas production processes to investigate syngas yield, CO_2 emissions and energy consumption. The identification of specific equilibrium-kinetic models for DRM is introduced in section 2. Conceptual designs and optimization of two types of syngas production processes are introduced. The first design is an ideal SMR+DRM process which can improve the syngas yield and suppress CO_2 emissions. The second design is a heat-integrated SMR+DRM process which can ensure the maximum heat recovery using the heat integration technique.

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To address almost net-zero CO_2 emission reduction, those conceptual designs are successfully verified by simulations in Aspen Plus environment.

II. SYNGAS PRODUCTION PROCESSES

The reaction of SMR and DRM are specified, respectively. For the SMR reactor, three exothermic or endothermic reactions are shown as follows :

$$CH_4 + H_20 \leftrightarrow CO + 3H_2\ (r_{SMR,1}),\ \Delta H^o_{298} = 206.2\text{ kJ/mol} \quad (1)$$

$$CO + H_20 \leftrightarrow CO_2 + H_2\ (r_{SMR,2}),\ \Delta H^o_{298} = -41.2\text{ kJ/mol} \quad (2)$$

$$CH_4 + 2\ H_20 \leftrightarrow CO_2 + 4H_2\ (r_{SMR,1}),\ \Delta H^o_{298} = 165\text{ kJ/mol} \quad (3)$$

The kinetics of SMR on a $Ni/MgAl_2O_4$ catalyst have been developed by using the Langmuir – Hinshelwood – Hougen – Watson (LHHW) as follows [1, 20]:

$$r_{SMR,1} = \frac{4.22\times10^{15}}{Den^2}\exp\left(\frac{240.1}{RT}\right)\left(\frac{P_{CH_4}P_{H_2O}}{{P_{H_2}}^{2.5}} - \frac{{P_{H_2}}^{0.5}P_{CO}}{K_1}\right) \quad (4)$$

$$r_{SMR,2} = \frac{1.995\times10^{6}}{Den^2}\exp\left(\frac{37.13}{RT}\right)\left(\frac{P_{CO}P_{H_2O}}{{P_{H_2}}^{2.5}} - \frac{{P_{CO_2}}^{0.5}}{K_2}\right) \quad (5)$$

$$r_{SMR,3} = \frac{1.02\times10^{15}}{Den^2}\exp\left(\frac{243.9}{RT}\right)\left(\frac{P_{CH_4}{P_{H_2O}}^{2}}{{P_{H_2}}^{3.5}} - \frac{{P_{H_2}}^{0.5}P_{CO_2}}{K_1K_2}\right) \quad (6)$$

$$K_1 = \exp(-26830/T + 30.114) \quad (7)$$

$$K_2 = \exp(4400/T - 4.036) \quad (8)$$

$$Den = 1 + 8.23\times10^{-5}\exp\left(\frac{-70.65}{RT}\right)P_{CO} + 6.12\times10^{-9}\exp\left(\frac{-82.9}{RT}\right)P_{H_2} + 6.65\times10^{-4}\exp\left(\frac{-38.28}{RT}\right)P_{CH_4} + 1.77\times10^{5}\exp\left(\frac{88.68}{RT}\right)\left(\frac{P_{H_2O}}{P_{H_2}}\right) \quad (9)$$

The DRM process has a rather complex reaction network since CO_2 is treated as a raw material at very high operating temperature [6, 18]. To address the kinetics of the DRM reaction, first the reduction of reaction mechanism is necessary [3] and second the feasible rate equation need to be identified [2]. By our approach, the primarily reactions of DRM are assumed as :

$$CO_2 + CH_4 \leftrightarrow 2\ CO + 2H_2\ (r_{DRM,1}),\ \Delta H^o_{298} = 247.2\text{ kJ/mol} \quad (10)$$

$$CH_4 + H_20 \leftrightarrow CO + 3H_2\ (r_{DRM,1}),\ \Delta H^o_{298} = 206.2\text{ kJ/mol} \quad (11)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O\ (r_{DRM,1}),\ \Delta H^o_{298} = 41.2\text{ kJ/mol} \quad (12)$$

$$CH_4 \leftrightarrow C + 2\ H_2\ (r_{DRM,2}),\ \Delta H^o_{298} = 75.6\text{ kJ/mol} \quad (13)$$

Meanwhile, the kinetics for DRM on a highly active $Ni/Rh/Al_2O_3$ catalyst are:

$r_{DRM,1} = (1.35\times10^{-7}\exp\left(\frac{529.2}{RT}\right)P_{CO_2}P_{CH_4} + 2.61\times$ 10−3exp144.3RTPCO2)−1×7.22×10−8exp(−372.9RT)PCO2 PCH4 (14)

$$r_{DRM,2} = 6\times10^{13}\exp\left(\frac{230100}{RT}\right)\frac{P_{CH_4}P_{H_2O}}{{P_{H_2}}^{2.5}} - 3\times10^{-9}\exp\left(\frac{17036}{RT}\right){P_{H_2}}^{0.5}P_{CO} \quad (15)$$

$$r_{DRM,3} = 1.875\times10^{-3}\exp\left(\frac{60000}{RT}\right)\frac{P_{CO}P_{H_2O}}{P_{H_2}} - 2.8\times10^{-2}\exp\left(\frac{85682}{RT}\right)P_{CO_2} \quad (16)$$

$$r_{DRM,4} = 6\times10^{3}\exp\left(\frac{60000}{RT}\right){C_{CH_4}}^{2} \quad (17)$$

The DRM process was attractive from the environmental and economical viewpoint owing to the potential utilization of greenhouse gases as resources, but it is still not commercialized. To emphasize the merits of DRM, comparisons of SMR and DRM according to syngas yield, energy consumption and CO_2 reduction are necessary. First, the reactor specifications presented in Table 1 and process configurations shown in Fig. 1(a) and 2(b) are the same. Second, the operating conditions of SMR and DRM, e.g. the inlet/outlet operating conditions with 298 K and 1 atm, are the same. Fig. 2(a) shows that the high H_2O/CH_4 ratio (>4) for the SMR at the high operating temperature (> 900K) can ensure H_2-rich syngas production rate, but Fig. 2(b) shows that the high ratio of CO_2/CH_4 (>4) for the DRM at the higher operating temperature (> 1200K) can ensure CO-rich syngas production rate.

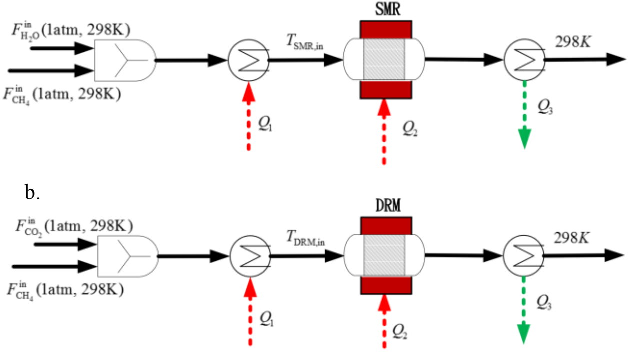

Figure 1. Syngas production processes: (a) SMR; (b) DRM

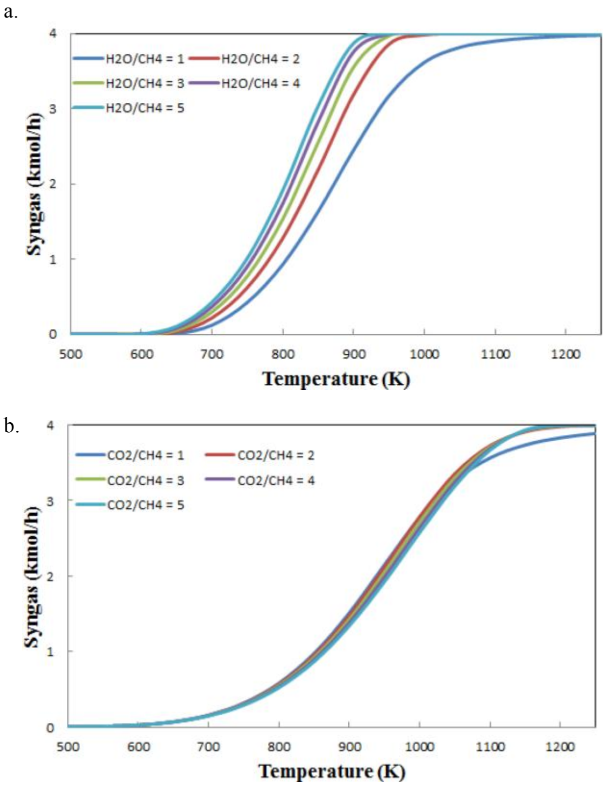

Figure 2. Syngas production processes: (a) SMR; (b) DRM

III. PROCESS INTEGRATION AND OPTIMIZATION

The design, optimization and simulation of two types of syngas production processes are investigated as follows.

A. *Ideal SMR+DRM Process*

An ideal SMR+DRM process (Design I) is presented and depicted in Fig. 3. Three individual inlet flows of CH_4, H_2O and CO_2, are mixed by a mixer and then fed into a series combination of SMR and DRM units. Two heater (HU_1, HU_2) are added to regulate the inlet temperatures of SMR and DRM, $T_{SMR,in}$ and $T_{DRM,in}$, respectively. A vapor–liquid separator (VLFD) is used to remove water in the inlet stream of DRM. Notably, the inlet/outlet temperatures of VLFD are assumed at 323K, and a cooler (CU_1) is used to cool down the outlet stream of SMR. Since both SMR and DRM require external energy supply, the external heat sources via heating jackets aim to execute the isothermal processes. Based on the specifications in Table 1, the optimal operating conditions are determined by solving the constrained optimization algorithm.

$$\max_{u_I} J_I = \mathrm{Syn}_{out} \frac{F_{syngas}{}^{out}}{F_{CH_4}{}^{in}} \tag{18}$$

subject to :

$$a_i \le u_{I,i} = [F_{CO_2}{}^{in}, F_{CH_4}{}^{in}, F_{H_2O}{}^{in}, T_{SMR,in}]^T \le b_i, i = 1, \ldots, 5 \tag{19}$$

$$CO_{2,out} \times \frac{F_{CO_2}{}^{out}}{F_{CH_4}{}^{in}} \le 0.01 \tag{20}$$

$$\frac{F_{H_2}{}^{out}}{F_{CO}{}^{out}} = y \tag{21}$$

where u_I represents adjustable variables. The syngas yield, Syn_{out}, is denoted as the objective (J_1) of Design I. Using the sequential quadratic programming (SQP) method in the Aspen Plus environment, the optimal solutions in Table 1 are obtained by solving the optimization algorithm subject to specific constraints in Eq. (14). These constraints include the measure of CO_2 emissions, $CO_{2,out}$, in the outlet, the upper and lower bounds of corresponding variables, a_i and b_i, and the prescribed ratio of $F_{H_2}{}^{out}$ to $F_{CO}{}^{out}$. Notably, $T_{DRM,in}$ is directly fixed at the upper bound of temperature, 1250K, in order to keep the best performance for the syngas production in the DRM. Moreover, the sensitivity analysis of this deal SMR+DRM process with regard to Syn_{out} and $CO_{2,out}$ is depicted in Fig. 4. Fig. 4(a) shows that the syngas yield and CO_2 emissions would simultaneously decrease if the CH_4 feed is higher than 7 kmol/h, Fig. 4(b) shows that CO_2 emission would rapidly increase if the CO_2 feed is higher than 4.1 kmol/h, Fig. 4(c) shows the syngas yield and CO_2 emission would simultaneously increase if the water feed continuously increases, and Fig. 4(d) shows that CO_2 emissions would rapidly increase if $T_{SMR,in}$ is higher than 860K. To meet the above optimization algorithm with specific constraints $CO_{2,out} \le 0.01$ and $y = 1.5$, four optimal operating conditions, $F_{CO_2}{}^{in}, F_{CH_4}{}^{in}, F_{H_2O}{}^{in}, T_{SMR,in}$, can be found in these figures. The optimal operating conditions at different ratios of y for Design I is shown in Table 2. Although the optimization of Design I can achieve the maximum syngas yield as well as very low CO_2 emissions, the external energy demand by hot/cold utilities (Q_H and Q_C) is quite large. Furthermore, the heat integration design is added to improve the energy consumption of this ideal SMR+DRM process.

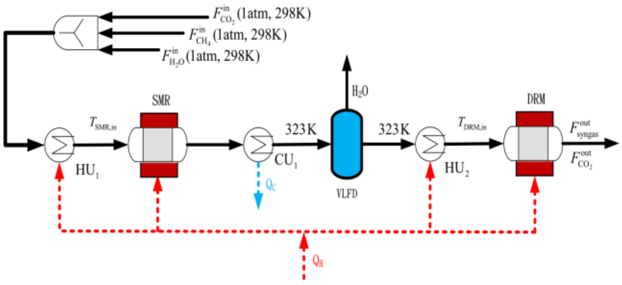

Figure 3. An ideal SMR+DRM process with prescribed operating variables

B. *Heat-integrated SMR+DRM Process*

The pinch analysis is used to explore the minimum energy consumption or maximum heat recovery for heat integration. The composite curves generated by mass flow rate and temperatures for four hot streams and four cold streams are depicted in Fig. 5(a). It shows that the minimum temperature difference between the hot and cold streams, e.g. ΔT_{min}=10 K, can be found, and the cooling duty by cold utility is quite small. To address the maximum heat recovery design, Fig. 5(b) shows that a heat-integrated SMR+DRM process (Design II) is presented. Notably, the feed flow is preheated by one of heat exchangers (EX1), and the outlet product flow is cooled down by another heat exchanger (EX2). If the outlet temperature of SMR (T_1) is close to the prescribed inlet temperature of VLFD at 323K, then Q_C is minimized to zero. If the outlet temperature of VLFD (T_2) is close to $T_{DRM,in}$, then Q_H can be effectively reduced. Apparently, both heat exchangers (EX1, EX2) should possess strong capability for heat transfer. Furthermore, the optimal operating conditions are obtained by solving the following optimization algorithm.

$$\min_{u_{II}} J_{II} = Q_C + Q_H \tag{22}$$

subject to :

$$a_i \le u_{II,i} = [T_1, T_2]^T \le b_i, i = 6, 7 \tag{23}$$

Notably, the sum of hot/cold duties is denoted as the objective (J_{II}) and u_{II} represents additional variables. Similarly, the upper and lower bounds of u_{II} are shown in Table 1. Based on the optimal conditions of u_I in Table 2, Table3 shows that the optimal operating conditions of u_{II} are determined. Obviously, the maximum heat recovery is achieved if T_1 is fixed at 323K. Compared to Design I, Design II can save over 40% energy consumption of hot/cold utilities.

TABLE I. MANIPULATED VARIABLES

Manipulated Variables	a_i	b_i
u_I		
$u_{I,1} = F_{CO_2}{}^{in}$ (kmol/h)	0	10
$u_{I,2} = F_{CH_4}{}^{in}$ (kmol/h)	0	10
$u_{I,3} = F_{H_2O}{}^{in}$ (kmol/h)	0	10
$u_{I,4} = T_{SMR,in}$ (K)	700	1000
$u_{I,5} = T_{DRM,in}$ (K)	850	1250
u_{II}		
$u_{II,6} = T_1$ (K)	298	373
$u_{II,7} = T_2$ (K)	850	1250

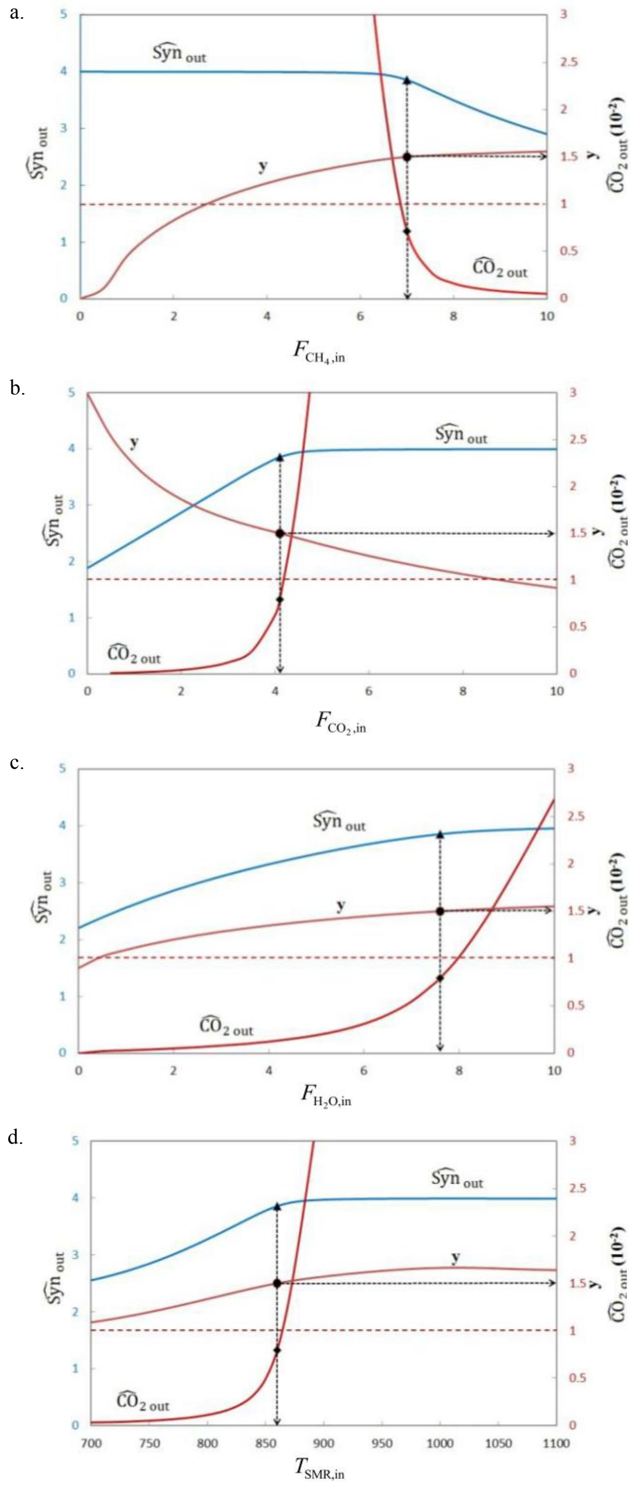

Figure 4. Optimization of an ideal SMR+DRM process by adjusting (a) CH_4 feed flow, (b) CO_2 feed flow, (c) H_2O feed flow, and (d) inlet temperature of DRM

TABLE II. OPTIMIZATION OF AN IDEAL SMR+DRM PROCESS

y	$F_{CO_2}^{in}$	$F_{CH_4}^{in}$	$F_{H_2O}^{in}$	$T_{SMR,in}$	Q_C	Q_H	Syn_{out}	$CO_{2,out}$
	kmol/h	kmol/h	kmol/h	(K)	(kW)	(kW)		(10^{-2})
1	8.5	8.7	0.9	750	102.3	975.1	3.87	0.90
1.5	4.1	7	7.6	860	168.9	894.5	3.86	0.71
2	3.0	9.2	7.6	1010	217.3	1149	3.84	0.57
2.5	1.1	7.9	8.9	980	182.9	989.6	3.80	0.36

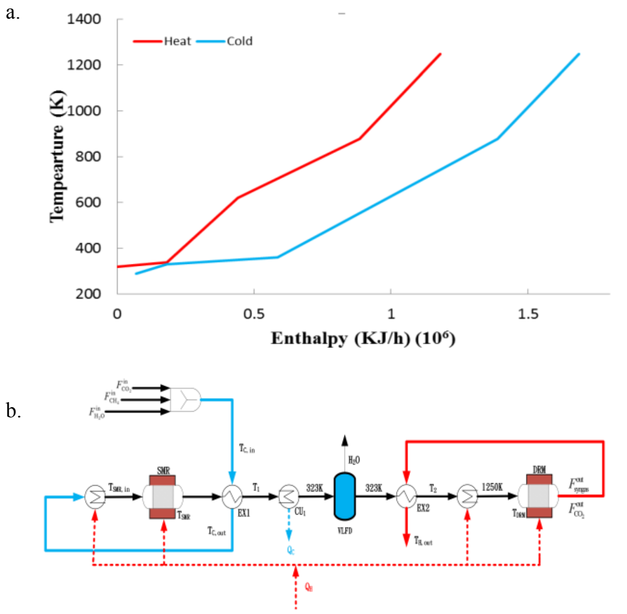

Figure 5. A heat-integrated SMR+DRM process: (a) temperature-enthalpy diagram; (b) simulation and optimization

TABLE III. OPTIMIZATION OF A HEAT INTEGRATED PROCESS

y	T_c^{in}	T_c^{out}	T_1	T_2	T_H^{out}	Q_C	Q_H
	(K)	(K)	(K)	(K)	(K)	(kW)	(kW)
1	285	695	323	1150	528	0	654.4
1.5	290	634	323	1145	501	0	544.7
2	290	794	323	1139	460	0	684.5
2.5	291	641	323	1142	459	0	595.9

IV. CONCLUSION

In this paper, we provide a CO_2 utilization technique to produce syngas and suppress greenhouse gas emissions. The first optimization algorithm for the ideal SMR+DMR process can ensure the higher product yield as well as lower CO_2 emissions than the sole SMR or DRM process. The second optimization algorithm for a heat-integrated SMR+DMR process can save over 40% energy. If the capital costs for renewable energy devices are acceptable, they may become an alternative option to replace the external heat demand by burning the hydrocarbon fuel in the proposed designs.

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