Article

A Polygeneration System Based on Multi-Input Chemical Looping Combustion [†]

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Abstract: This paper proposes a polygeneration system based on a multi-input chemical looping combustion system, which generates methanol and electricity, through the use of natural gas and coal. In this system, the chemical looping hydrogen (CLH) production system and the coal-based methanol production system are integrated. A high quality fuel, natural gas, is used to improve the conversion ratio of coal. The Gibbs energy of the two kinds of fuels is fully used. Benefitting from the chemical looping process, 27% CO_2 can be captured without energy penalty. With the same outputs of methanol and electricity, the energy savings ratio of the new system is about 12%. Based on the exergy analyses, it is disclosed that the integration of synthetic utilization of natural gas and coal plays a significant role in reducing the exergy destruction of the new system. The promising results obtained in this paper may lead to a clean coal technology that will utilize natural gas and coal more efficiently and economically.

Keywords: chemical looping; hydrogen production; multi-input fossil fuel; polygeneration
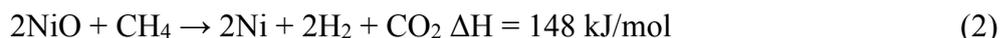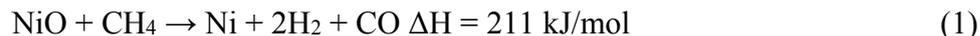
1. Introduction

Chemical production plants and power generation systems are usually constructed as independent systems. In a typical chemical production plant, heat generated by chemical processes is seldom coupled to other chemical processes requiring energy, resulting in high energy consumption. In the typical power plant, high exergy destruction from combustion processes, which accounts for about 30% of the total fuel exergy [1], limits the improvement of their thermal efficiency. These defects in energy use can potentially be overcome by polygeneration systems, a promising technology that is attracting increasing attention. A polygeneration system is one that integrates chemical production processes with a power generation system, and produces both chemical and electrical energy simultaneously. To date, a number of polygeneration systems of various configurations have been proposed [2–5], and several test projects have been funded for polygeneration plants in the USA and in China [2,3]. Most of the researches into polygeneration systems have focused on economic analyses and energy analyses [6,7], with a few focused on exergy analyses of polygeneration systems [8].

Polygeneration systems involve various fields of research, including chemistry, power generation, and even metallurgy. Polygeneration systems designed by chemical experts are inclined to pay too much attention to the chemical conversions being carried out, while polygeneration systems developed by the power generation experts tend to pay too much attention to thermal energy conversion. There is little research that has focused on the actual relationship between the chemical production processes and the power generation systems, or on integration of the polygeneration system based on systemic synthesis, such as comparative analyses of the low conversion and high conversion cases. In fact, decreasing the exergy consumption for the chemical conversion and then utilizing the fuel efficiently for combustion in the power generation system are the key factors that need to be understood in order to enhance the performance of the polygeneration system. The system integration needs to focus on both chemical conversion and thermal exergy conversion synergistically.
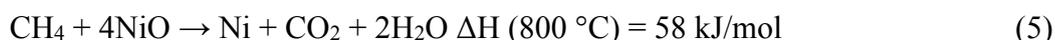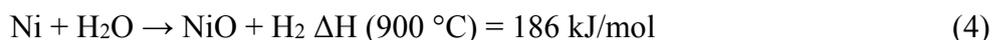
Chemical looping combustion (CLC) is a technique where the greenhouse gas CO_2 is inherently separated during combustion. To date, several researchers have investigated CLC [9–11], and a project for a novel CO_2 separation system has been conducted by the United States Department of Energy [12], while Sweden [13] and Korea [14] have developed 100 and 50 kW CLC power plants, respectively. The system consists of two reactors: an air reactor and a fuel reactor. Gaseous fuel is introduced into the reduction reactor, where it reacts with an oxygen carrier to produce CO_2 and H_2O. The reduced oxygen carrier is then transported to the air reactor, where it is oxidized back to its original form by air. A recent 1 MW_{th} chemical looping plant is reported by Ströhle [15]. A 25 kW_{th} CDCL (coal direct chemical looping) sub-pilot plant has been constructed and demonstrated successfully at Ohio State University with the support from National Energy Technology Laboratory (NETL) of the United States Department of Energy (USDOE) [16]. Hamburg University of Technology (Institute of Solids Process Engineering and Particle Technology) had a successful operation of a coupled fluidized bed system for CLC of coal using ilmenite as the oxygen carrier [17] in Germany. The carbon capture rate based on Australian ilmenite is higher than 96%.

Chemical looping reforming (CLR) produces hydrogen using the CLC principle [18,19]. The main reactions in CLR are as follows, with nickel used as Equations (1)–(3):

$$NiO + CH_4 \rightarrow Ni + 2H_2 + CO \; \Delta H = 211 \; kJ/mol \tag{1}$$

$$2NiO + CH_4 \rightarrow 2Ni + 2H_2 + CO_2 \; \Delta H = 148 \; kJ/mol \tag{2}$$

$$CH_4 + Ni \rightarrow C\text{–}Ni + 2H_2 \; \Delta H = 191 \; kJ/mol \tag{3}$$

The first reaction is considered as the primary pathway, whereas the other two reactions are possible reactions. Natural gas is used as fuel in CLR research. To supply enough heat to drive the reforming reaction on the fuel reactor side, part of the natural gas is burned directly to support the reaction.

Another method to produce hydrogen using CLC is water splitting applied to chemical looping (chemical looping hydrogen generation, CLH) [20]. The CLH process is based on two reactors. The CLH fuel reactor is similar to that used in CLC, but the CLC air reactor in is replaced with a steam reactor, in which steam reacts with the metal to produce hydrogen. In CLH, both sides of the reactions are endothermic. These reactions are as follows, Equations (4) and (5):

$$Ni + H_2O \rightarrow NiO + H_2 \; \Delta H \; (900 \; °C) = 186 \; kJ/mol \tag{4}$$

$$CH_4 + 4NiO \rightarrow Ni + CO_2 + 2H_2O \; \Delta H \; (800 \; °C) = 58 \; kJ/mol \tag{5}$$

Approximately 10% to 20% of natural gas is burned directly to supply the heat for the reactions in SMR (Steam Methane Reforming) and CLH systems.

This paper proposes a polygeneration system integrated with a CLH and coal gasification system. This multifunctional energy system (MES) uses a high quality fuel, natural gas, to improve the utilization of coal, through the chemical looping process. Its purpose is to reveal the mechanism of CLH and coal gasification using exergy-utilization diagram (EUD) methods, to disclose the cascade utilization of chemical energy and physical energy in the system, and to display the performance and CO_2 emission reduction of the system.

## 2. Description and Basic Idea of the Multifunctional Energy System (MES)

In a coal-based methanol production process, to increase the H_2/CO ratio of the syngas to 2.66, which will promise the highest methanol production, the shift reaction is adopted in the fresh gas preparation subsystem. Meanwhile, to reach a high conversion ratio of carbon in coal, the unreacted gas is compressed and recycled to mix with the fresh gas as a recycle stream. However, these measures cause significant exergy consumption, which deteriorates the critical processes in chemical production.

Natural gas, a high quality fuel, is a kind of hydrogen-rich gas, but natural gas is usually burned directly, which accounts for about 30% of the total fuel exergy. Meanwhile, the chemical looping combustion is a new method, which can decrease the exergy destruction of fuel and capture CO_2 without energy penalty. The MES use natural gas to adjust the H_2/CO ratio to improve the syngas preparation and increase the performance of the system through chemical looping process.

Figure 1 shows a flowchart of the MES system which includes four subsystems: a CLH subsystem, a syngas preparation subsystem, a methanol production subsystem, and a power generation subsystem. In the CLH subsystem, the nature gas is converted into hydrogen, CO_2 and other by-products. One ton of natural gas (about 25 GJ) can be converted into about 0.706 ton of hydrogen. The hydrogen generated in the CLH system is first cleaned up and then is sent to the methanol production system.

In the hydrogen production (CLH) subsystem, the natural gas and the water enter the heat exchanger. In the heat exchanger, the heat donor are the syngas from the gasification unit. Ni is chosen as the oxygen carrier [21]. The water and the natural gas, preheated from 25 to 1000 °C, act as the heat acceptor. Then, natural gas reacts endothermically with NiO and the catalyst in the reduction reactor. The endothermic reaction path is $CH_4 + 4NiO \rightarrow Ni + CO_2 + 2H_2O$ and absorbs 253 kJ of thermal energy per mole of CH_4 at 900 °C from the syngas which is produced in the gasification unit. In the steam reactor, the NiO is reduced into Ni in the reduction reactor before it enters the fuel reactor. In the steam reactor, Ni is oxidized with steam and catalyst as follows: $Ni + H_2O \rightarrow NiO + H_2$, which is also an endothermic reaction. The reaction absorbs 96 kJ of thermal energy per mole of CH_4 at 900 °C.

Figure 1. Scheme of the multifunctional energy system (MES).
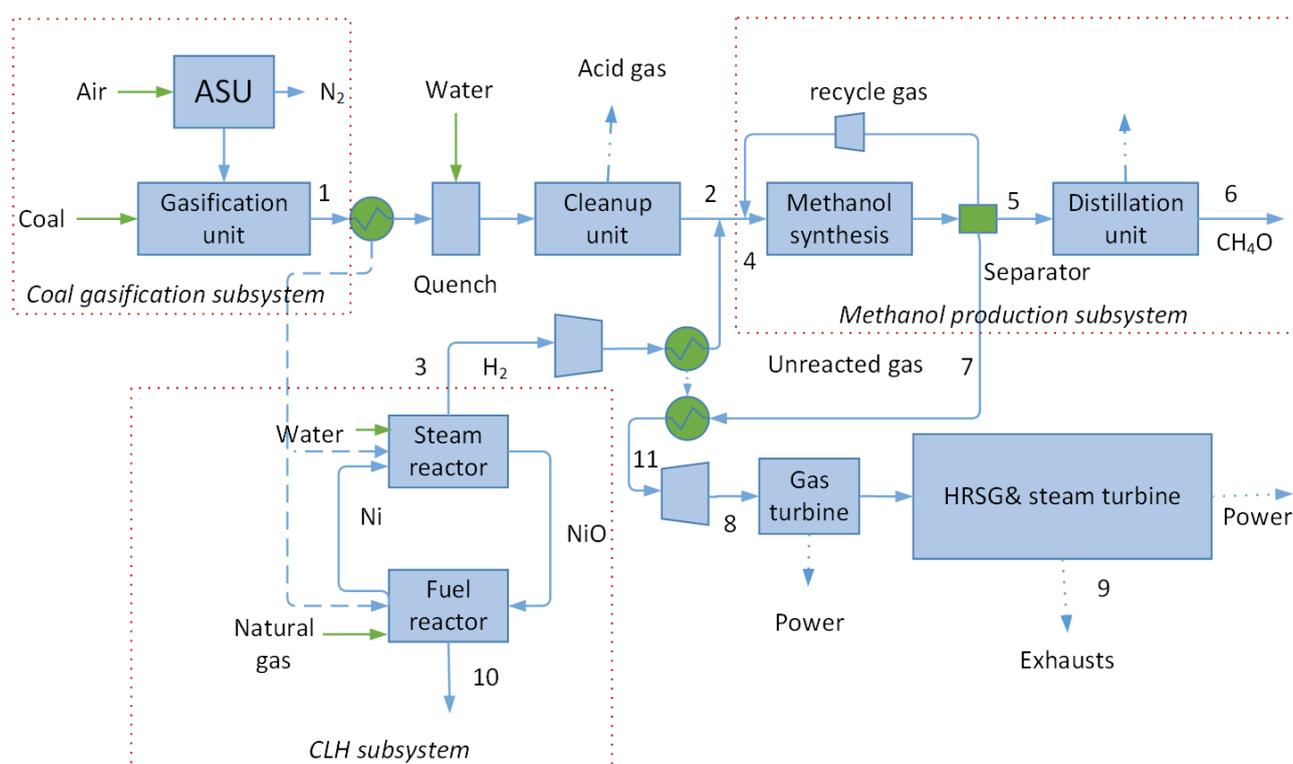
In the syngas preparation subsystem, coal is gasified at 1619 K and 68 bar by steam and oxygen, which is obtained from an air separation unit. For the gasifier, the oxygen consumption is about 0.86 kg oxygen per kg coal, and the ratio of the total lower heating value of cold produced gas to the total lower heating value of coal input is about 76.8%. The gas product leaving the gasifier cyclone enters a cleanup unit for removal of particulates and desulphurization, after being cooled to about 311 K in the product gas cooler. Then the syngas is mixed with clean hydrogen at the ratio of 1.1 by volume. After further cleanup, fresh gas for methanol synthesis can be obtained, which is free of components poisonous to the catalyst, and can then be sent to the methanol production subsystem as feedstock.

The methanol production subsystem is composed of a synthesis unit and a distillation unit. The MES system adopts a partial recycling scheme, recycling part of the unreacted gas back to the reactor. Methanol synthesis is simulated by specifying the temperature approach to real industrial data (the temperature approaching equilibrium was about 38 K [22]). At a pressure of 76 bar, the reactor is maintained at the temperature of 523 K by evaporation of the cooling water. The crude methanol and

unreacted gases are separated, after being cooled down to ambient temperature by a cooler, and crude methanol is then sent to a distillation unit. Part of the unreacted gas is cycled back to the reactor, and the other part is sent to the power generation subsystem (combined cycle). The power subsystem supplies the power and the steam that are required in the former processes.

3. Evaluation of the MES

### 3.1. Description of Reference Systems

With the multi-input of natural gas and coal and the multi-output of methanol and power, the evaluation of this MES system will be based on its comparison to single systems, which are the coal-based methanol plant and combined cycle. Figure 2 shows a typical coal-based methanol production process (M-C), which can be divided into two subsystems: a fresh gas preparation subsystem (to produce fresh gas for methanol synthesis from coal) and a methanol synthesis subsystem. The energy required by the methanol production process is obtained by recovering thermal energy in former processes and from a captive steam power plant with coal-fired boiler. The energy consumption is 45.6 GJ/t-CH_4O, which is almost the same as the industry data [23].

Figure 2. Flow diagram of coal-based methanol production.
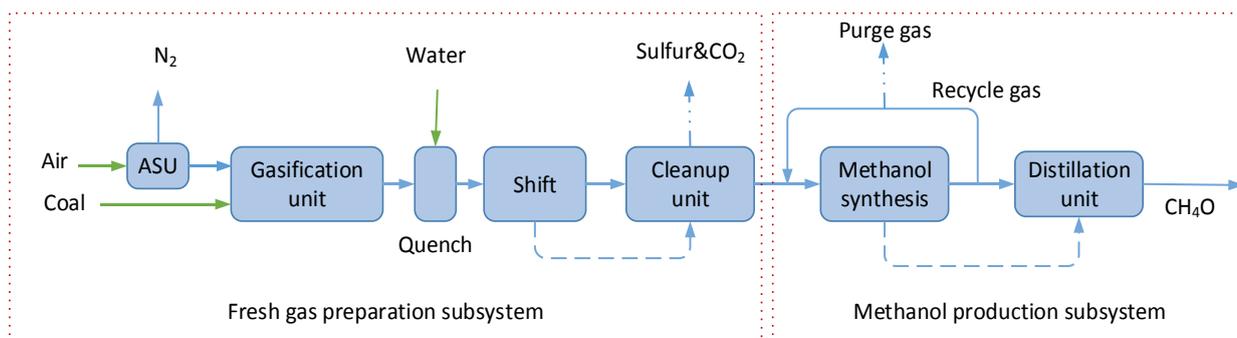
In the combined cycle (Figure 3), natural gas is combusted with compressed air from the compressor in the combustion chamber. The high-temperature gas is introduced to a gas turbine to generate electricity, and then the thermal energy of the exhaust gas of gas turbine is recovered by a steam cycle with a dual-pressure HRSG (Heat Recover Steam Generator) and steam turbine.

Figure 3. Flow diagram of combined cycle.
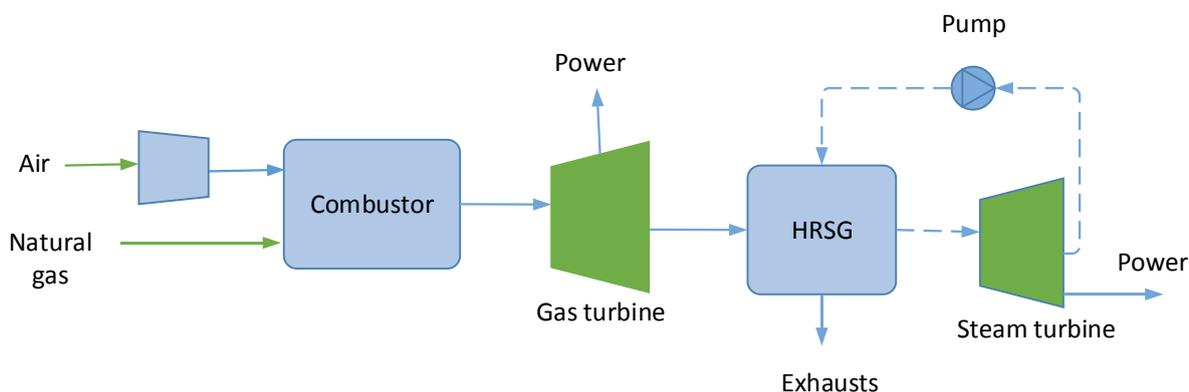
Based on the simulation result, its thermal efficiency is 58.2%. The definition of the energy saving ratio (ESR) is as following:

$$ESR = (Q_{ref} - Q_p)/Q_{ref} \tag{6}$$

here Q_p is the total energy input (LHV) in the MES system and Q_{ref} is that in the reference system with the same outputs as those of the MES.

3.2. Evaluation of the MES

In the MES system, the CLH subsystem is based on the chemical looping combustion, which can capture CO_2 without energy penalty [9]. The power subsystem is based on a heavy-duty gas turbine (GE model MS 206FA, General Electric Company, Atlanta, GA, USA, which was selected according to the scale of the system) of current technology with a turbine inlet temperature of 1561 K and a pressure ratio of 15. The steam, which is saturated at the pressure of 12 MPa and is reheated at the pressure of 3.9 MPa, is generated in a HRSG. The temperatures of both the superheated and reheated steam are 811 K. The main assumptions of the reference systems and MES are based on industrial data. For example, The data of the methanol plant specifications came from the Tianjian project in Tianjin, China which operated in 2012, and produce methanol about 500,000 ton per year. The ASU (Air Separation Unit) parameters are based on [24].

The MES system was studied through the commercial software, Aspen Plus (Aspen Technology, Bedford, MA, USA). STEAM-TA method is used in the simulation of steam cycle, while SOLIDS and PENG-ROB method is selected in solid cycle and gas cycle. Chemical reactors were simulated in Aspen Plus using RGibbs blocks, which simultaneously model the chemical and phase equilibrium by minimizing the Gibbs free energy of the reactor products, subject to atomic balance constraints. During the evaluation, the elemental chemical composition of coal (wt%) was assumed as follows: 68.54% C, 3.97% H, 6.85% O, 0.74% N, 1.08% S, 9.98% ash, and 8.84% water, and its lower heating value (LHV) was 26,710 kJ/kg. The pressure, temperature, mass flow, and composition of the main points in Figure 1 are listed in Table 1.

Table 1. Parameters of the main points of the MES system.

Point	G	P	T	Percent molar composition (%)								
	Kmol/s	bar	°C	CH$_4$	C$_2$H$_6$	CH$_4$O	CO	CO$_2$	H$_2$	H$_2$O	O$_2$	N$_2$
1	0.578	68	1346	0.1	-	-	44.1	10.5	30.8	12.7	-	1.6
2	0.554	65	38	0.1	-	-	50.5	12.1	35.4	0.1	-	1.9
3	0.548	1.03	900	-	-	-	-	-	100	-	-	-
4	0.918	62	38	0.1	0.2	-	30.5	8.4	61.0	0.1	0.2	5.2
5	0.181	74.5	40	0.2	2.8	92.7	1.4	0.4	0.2	0.3	0.2	0.7
6	0.168	4.9	110.4	-	-	99.6	-	-	-	0.4	-	-
7	0.413	73.7	53	0.1	2.1	0.4	22.1	18.6	44.2		2.2	10.2
8	0.413	15.4	81	0.1	2.1	0.4	22.1	18.6	44.2		2.2	10.2
9	9.217	1.02	120	-	-	-	-	3.9	-	7.5	13.1	75.4
10	0.411	1.02	110	-	-	-	-	0.33	-	0.67	-	-
11	0.413	73.7	314	0.1	2.1	0.4	22.1	18.6	44.2	-	2.2	10.2

The performance comparisons of the MES system to those of the reference systems are shown in Table 2. It shows that the overall efficiency of the MES system is about 57.6%, which is 7.2 percentage points higher than the combined overall efficiency of the reference systems. The energy saving ratio of the MES system is as high as 12.3%. With the same outputs, the coal consumed by the MES is 304 MW and the natural gas is 106 MW. Comparing with the reference systems, the coal consumption in the MES system increased by 22.5%, but the natural gas consumption decreased by 52%. The contribution to the high performance by replacing combined cycle with CLH system is about 3.6 percentage points; the contribution by removal of the shift reaction is about 2.5 percentage points; and the contribution for the thermal integration is about 1.1 percentage points.

Table 2. Results for the new MES system and reference systems.

Item	MES	Reference systems		
		Total	Coal-methanol	Combined cycle
Input (MW)				
Coal	304	248	248	-
CH$_4$	106	220	-	220
Output (MW)				
Electricity	128	128	-	128
Methanol	108	108	108	-
Thermal efficiency (%)	57.6	50.4	43.7	58.2
Energy saving ratio (%)	12.3	-	-	-

The exergy analyses in Table 3 indicate that the decrease in exergy destruction is mainly located in the coal gasification unit and the syngas preparation unit in the MES system, compared to those of the reference systems.

Table 3. Exergy analyses of the MES and reference systems.

Item	MES (MW)	Reference systems (MW)		
		Total	Coal-methanol	Combined cycle
Coal input	307	251	251	-
Nature gas input	109	223	-	223
ASU	6.7	6.7	6.7	-
Gasification	29.8	29.8	29.8	-
Crude gas cooling	6.2	11.1	11.1	-
Shift	-	25.6	25.6	-
Fuel and steam reactor	9.3	-	-	-
Methanol synthesis	8.3	15.0	15.0	-
Distillation unit	10.2	11.9	11.9	-
Air compressor	5.8	5.8	-	5.8
Combustion for power	55.9	84.2	41.5	42.7
Gas turbine	5.1	5.4	-	5.4
Steam turbine	8.6	8.9	3.7	5.2
HRSG and exhausts	19.2	22.1	6.2	15.9
Auxiliary	0.9	0.7	0.7	-
Electricity outputs	128	128	-	128
Methanol outputs	122	122	122	-
Total	416	474	251	223

In the MES system, the sensible heat of syngas is first used to drive the CLH subsystem to produce hydrogen. Then the syngas at a temperature of 400–500 °C is cooled by water. Because the MES system realized reasonable use of sensible heats of syngas instead of quench, the exergy destruction in the crude gas cooling was decreased from 11.1 to 6.2 MW. Compared with the reference systems, the MES system eliminated the shift reaction instead of chemical looping hydrogen production reaction, so the exergy destruction decreased 16.3 MW (from 25.6 to 9.3 MW), which accounted for about 3.8% of the total exergy inputs in the MES system. The exergy destruction for the combustion (including natural gas and unreacted gas combustion) decreased from 84.2 MW in the reference systems to 55.9 MW in the MES system, because of the elimination of the natural gas combustion in combined cycle. Totally, comparing with the reference systems, the exergy destruction of MES system decreased 53.4 MW, about 12% of the total exergy inputs.

4. Discussion

With the development of complex cycles including complicated chemical/thermal processes, many researchers have paid close attention to the exergy principle for analysis, optimization, and synthesis of the thermal/chemical systems. In order to reveal the internal phenomena of the key processes in the new system, the graphical exergy analysis (EUD methodology), proposed by Ishida [11], was adopted. The EUD methodology we used here focuses graphically on the energy level difference in a pair of energy donor and energy acceptor. Both the variation of energy level and energy quantity are graphically shown with $A - \Delta H$ coordinates. Here, the energy level A is a dimensionless criterion ($A = \Delta\varepsilon/\Delta H = 1 - T_0 \times \Delta S/\Delta H$, a ratio of exergy change to energy change), and the energy quantity ΔH refers to any kind of energy changes, such as thermal energy, power consumption or generation, and energy change in chemical reaction, *etc.*

The *x*-coordinate in the EUD is energy change, and the y-coordinate is energy level A. For an energy-transformation process, there exists an energy donor and an energy acceptor, so the exergy destruction is illustrated by the shaded areas between the curves of the energy donor and energy acceptor. In this way, the EUD methodology has particular advantages over conventional exergy methods in showing: (i) the energy level degradation in each process, instead of only magnitudes of exergy losses obtained from the exergy value difference between the output and input of units; (ii) the variation of driving force by dividing the whole process into infinitive processes; (iii) both global and special information on different phenomena such as work, thermal and chemical processes. Hence, the EUD methodology may provide information on the feasibility of process, driving force, defect points, and potential of improvement from intuitive and global viewpoints [12].

4.1. Significance of the Chemical Looping Hydrogen Production Process in the MES System

To disclose the role of CLH process in the MES system, we compare the two different ways of using natural gas. In the reference systems, the natural gas is burned directly, which causes a big exergy destruction. The MES system uses chemical looping process to decrease the exergy destruction in the utilization process of natural gas. Instead of shift reaction, the MES system just simply mixed the syngas with hydrogen to reach the CO/H_2 ratio. Meanwhile, the energy level of syngas sensible heat is a little

higher than the CLH reaction level. The heat is used to drive the fuel reaction and steam reaction in CLH subsystem.

Figure 4a shows the exergy destruction distribution for the combustion of coal in the coal-fired coke oven and the gasification of coal in the gasifier of the MES system. In the CLH subsystem, the syngas acts as the energy donating reaction (curve A_{ed1}), and the reactions in fuel and steam reactors are the energy accepters (curve A_{ea1}, A_{ea2}).

The right part of Figure 4a shows the exergy destruction of coal gasification process. The coal is the energy donor (curve A_{ed2}) and the three streams (curve A_{ea3}, A_{ea4} and A_{ea5}), which act as energy acceptors, are the preheating of water, the preheating of air, and the preheating of coal. The A_{ea6} is the reaction level of gasification. The exergy destruction is equivalent to the area between the curves of the energy donor and the energy acceptors, which is 55.9 MW.

Figure 4. (**a**) EUD for combustion and gasification in the MES; (**b**) EUD for combustion and gasification in reference systems.
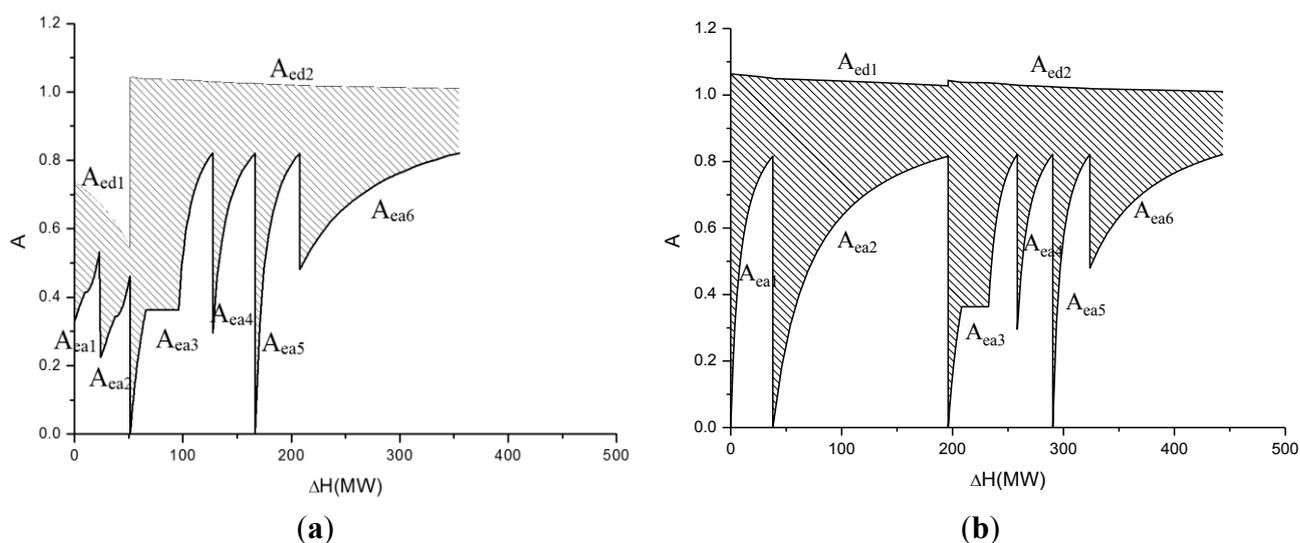

(**a**) (**b**)

Figure 4b contrasts the combustion of natural gas in the combined cycle and the exergy destruction distributions of the coal gasification in the coal based methanol production system. Curve A_{ed1} represents the combustion of natural gas, which acts as an energy donating reaction in the combined cycle, and two streams (curve A_{ea1}, and A_{ea2}) act as energy acceptors: the preheating of natural gas and air. The exergy destruction for the combustion of natural gas is 42.7 MW (the shaded area below the curve and of A_{ed1} and A_{ea1}, A_{ea2}). For the coal gasification process, which is the same as Figure 4a, shows the exergy destruction in the gasifier is 41.5 MW. Moreover, the thermal energy quantity (ΔH) between the energy donor and the energy acceptor in the MES (355 MW) was also less than that in the reference systems (444 MW). Therefore the total exergy destruction of combustion and gasification in the reference systems is about 84.2 MW. Comparing Figure 4a with Figure 4b, it is clear that the CLH subsystem not only decreases the exergy destruction of natural gas utilization, but also use the sensible heats of syngas reasonably. This is the main reason why the MES system has a much higher performance than reference systems.

4.2. The Elimination of Shift Process and Thermal Integration

There are two different ways to adjust the CO/H_2 ratio in the MES and reference systems. In the coal-based methanol production system, the syngas is divided into two streams before the shift unit: one stream about 56%, called "shift gas", is sent to the shift unit to adjust the CO/H_2 ratio to 2.66 via a water–gas shift reaction; and the rest, named "mixed gas", bypasses the shift unit. The shifted gas combines with the mixed gas after the shift unit. A quenching unit is designed to cool all of the raw syngas leaving the gasifier from about 1619 to 513 K. Before entering the cleanup unit, a heat recovery unit is added to recover the middle temperature heat of the syngas.

From Table 3, it is clear that the exergy destruction of shift process is 25.6 MW, but the MES decreases this destruction by mixing hydrogen with syngas. Meanwhile, the sensible heat of syngas is used to produce hydrogen as it is. The MES makes the best use of CLH process, and have a high energy saving ratio.

4.3. Advantages for CO_2 Capture and Further Considerations

The MES system can effectively use natural gas and coal. In the power subsystem, the conventional steam turbine can be adopted without modification. The gas turbine needs only a slight modification in order to be adapted for purge gas, and this is not a technological obstacle. The liquid phase methanol technology (LPMEOH) that exists today is fit for the methanol synthesis unit in the MES system [13].

With the same outputs, the fuel inputs of the MES system are about 12.3% less than those of the reference systems, because of the high performance of the MES system. If the CO_2 is not captured, the CO_2 emission ratios of MES and the reference system are 0.177 kg/MJ-output and 0.185 kg/MJ-output. Therefore, the emissions from the MES system would be at least 5% less than those of the reference system. Because of the advantage of CO_2 capture without penalty in chemical looping combustion, the MES can capture 27% of the total CO_2, which can be captured from the stream 10 in Figure 1. To gain this reduction, the MES system need not add new equipment or increase the energy consumption, because the CO2 is just mixed with steam and it can be separated easily by cooling the steam to liquid. In other words, the MES system is far more environmentally friendly. Based on the CLH system, many different multifunctional energy systems, such as the co-generation of hydrogen, power, and other chemical products (DME) can be constructed with this basic framework, allowing this kind of CLH process to be used as a new method for the efficient utilization of coal.

5. Conclusions

A multifunctional energy system which can utilize natural gas and coal more effectively through the synthetic utilization of natural and coal was analyzed. Based on the integration of a chemical looping hydrogen production process and a coal-based methanol production system, the fuel and thermal energy were utilized efficiently from the viewpoint of the whole system.

Graphical exergy analyses (EUD methodology) revealed that the natural gas and coal were utilized synthetically through the CLH system. The input natural gas/coal ratio is 1:3. The advantage of the natural gas, rich hydrogen, is fully used to decrease the exergy destruction of methanol production. The energy saving ratio of the MES can reach 12.3% and can save 50% natural gas. The exergy analysis

shows that the performance increase is mainly caused by the reasonable utilization of natural gas through CLH system instead of natural gas burning. Benefits from the chemical looping process, the 27% of CO_2 can be captured without energy penalty. Also the elimination of shift process and thermal integration are the reasons why the MES has a high performance. This versatile MES system not only improves the overall efficiency, but also reduces CO_2 emissions.

Acknowledgments

Author Contributions

Sheng Li contributed significantly to analysis and manuscript preparation. Hongguang Jin helped perform the analysis with constructive discussions.

Conflicts of Interest

The authors declare no conflict of interest.

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