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Progress of energy system with chemical-looping combustion

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Chemical-looping combustion with zero energy penalty of CO_2 separation is a significant breakthrough in resolving energy and environment problems for power generation systems. This paper summarizes the research on energy systems with chemical-looping combustion conducted in recent years, discloses the underlying mechanism of energy release of chemical-looping combustion, describes the trends of the key technology development, and presents the proposed chemical-looping combustion thermal cycles. This paper may provide a new direction to the synthesis of the next-generation energy system compatible with environment.

chemical-looping combustion, CO_2 separation, energy-environment system

The compatible development of both the efficient energy utilization and environment protection is the hottest and most difficult problem in the 21st century. The effort of reducing CO_2 emission has been a key factor of decision-making for all the countries' energy policies. So far, the main difficulty of CO_2 recovery for power systems needs extra energy penalty for the separation of the amount of CO_2, which greatly decreases the thermal efficiency by 5%—15%. It is due to the fact that CO_2 of the flue gas from the fossil fuel combustion is usually diluted by N_2. In addition, the traditional approaches of both "treatment after pollution" and "environment after energy conversion" also give rise to more energy consumption and increasing pollutants. That is to say, the traditional approaches of solving energy crisis and environmental pollution are yet confined to the scope of individual discipline, rather than breaking the boundary. Therefore, from the viewpoint of scientific crossing between energy and environment, it is urgent to break the binding of traditional idea and to find out a practicable approach to resolve energy utilization and environment pollution simultaneously[1].

It has been found from our research that there are close interactions between energy utilization and CO_2 separation, and they are not independent. At present, the largest energy destruction in power system takes place in the fossil combustion process where the chemical energy of fuel is converted into physical energy. In this way, almost 30% of the chemical energy contained by the fuel will be destructed. On the other hand, the combustion process is also the source of the generation of CO_2 as well as the conversion process involving chemical energy. Therefore, the combustion process has great potential in simultaneously solving energy utilization and environment pollution problems, and may be an effective breakthrough in the CO_2 recovery for power systems[2].

In 1994, Ishida and Jin originally proposed a novel chemical-looping combustion (CLC) thermal cycle with inherent CO_2 separation[3]. They first explored a new approach of integrating energy conversion and CO_2 separation from the synergistic chemical-l- ooping combustion with thermal cycle. This research result was patented in USA[4]. Figure 1 illustrates the saturated air gas turbine cycle with natural-gas fired chemical-looping combustion (CLSA). The natural-gas fired chemi-

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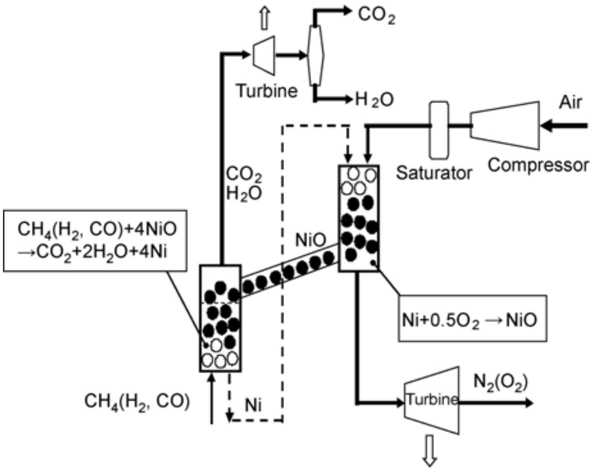

Figure 1 Schematic illustrating the concept of chemical-looping combustion.

cal-looping combustion decomposes the conventional direct-combustion of methane into two gas-solid reactions. In the first reduction reactor (fuel reactor), methane reacts with a metal oxide NiO to produce the metal Ni. The compressed air from the intercooler is saturated in a saturator, and is fed into the second oxidation reactor (air reactor), in which the reduced product Ni reacts with the oxygen contained in air to be oxidized to NiO. The metallic oxide (MeO) is repeatedly used and plays the role of an oxygen carrier between the two reactors.

Fuel reactor:

$$C_xH_y+(2x+y/2)MeO = xCO_2+(y/2)H_2O+(2x+y/2)Me. \tag{1}$$

Air reactor:

$$(2x+y/2)Me+(x+y/4)O_2 = (2x+y/2)MeO. \tag{2}$$

The gas product discharged from the reduction reactor consists mainly of CO_2 and water vapor. The produced CO_2 is not diluted by air since air and fuel enter different reactors. In this way, using the simple condenser method can separate CO_2 from water without any extra energy penalty and special separator device. The investigation results show that the proposed system is expected to have an advanced thermal efficiency, eight percent higher than that of conventional combined cycle. This advantage benefits from the fact that chemical-looping combustion is capable of decreasing the destruction of chemical energy through degrading the energy level of the released fuel and accomplishing zero energy for CO_2 separation. That is to say, the proposed system can unite the high efficient utilization of chemical energy of fossil fuel with the CO_2 separation without any extra energy penalty. The Intergovernmental Panel on Climate Change Report[5] especially pointed out: "with subsequent contributors by Ishida and Jin (1994), the main idea of chemical-looping combustion is to spit combustion of hydrocarbon or carbonaceous fuel into separate oxidation…..".

Since then, some institutions in European and American countries have been attaching importance to the role of chemical-looping combustion on the CO_2 capture, such as Chalmers University of Technology in Sweden, Royal Institute of Technology in Sweden, Norwegian University of Science and Technology (NTNU) in Norway and Instituto de Carboquı´mica (CSIC) in Spain, and so on. Since 1992, the number of the published papers on the study of chemical-looping combustion has increased by 10 times, as shown in Figure 2. In the 21st century, the research of energy system with CO_2 capture by using chemical-looping combustion is initiating a climax. Several international organizations and countries take the energy system with chemical-looping combustion as the most important and prospective strategic choice of CO_2 capture. Especially in the latest years, Europe and USA. etc. have vigorously developed pilot projects of chemical-looping combustion to accelerate its industrialization, e.g., the GRACE project of FP5[1)], and Enhanced Capture of CO_2 project[2)] and Chemical Looping Combustion CO_2-Ready Gas Power[3)] project of FP6 supported by EU. The prototype of 10 kW_{th} fluidized bed chemical-looping combustor has been devel-

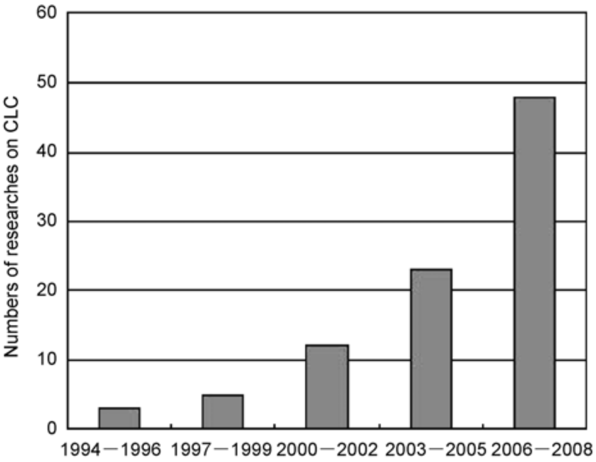

Figure 2 Status of the published paper on CLC.

[1)] http://cordis.europa.eu/data/PROJ_FP5/ACTIONeqDndSESSIONeq112362005919ndDOCeq894ndTBLeqEN_PROJ.htm

[2)] http://cordis.europa.eu/fetch?CALLER=FP6_PROJ&ACTION=D&DOC=1&CAT=PROJ&QUERY=011a5ceb860c:a0a2:0dc7873e&RCN=73993

[3)] http://cordis.europa.eu/fetch?CALLER=FP6_PROJ&ACTION=D&DOC=2&CAT=PROJ&QUERY=011a5ceb860c:a0a2:0dc7873e&RCN=78507

oped by Chalmers University of Technology[6] and a 50 kW_{th} chemical-looping combustion power plant has been constructed in Korea. The largest chemical-looping combustion power plant (100 kW_{th}) of the world is being set up and supported by the BIGCO2 with the biggest research project of Europe, as shown in Figure 3[7]. At present, the design and construction of a small transparent cold demonstrator CLC rig is completed in the SINTEF ER/NTNU EPT laboratory.

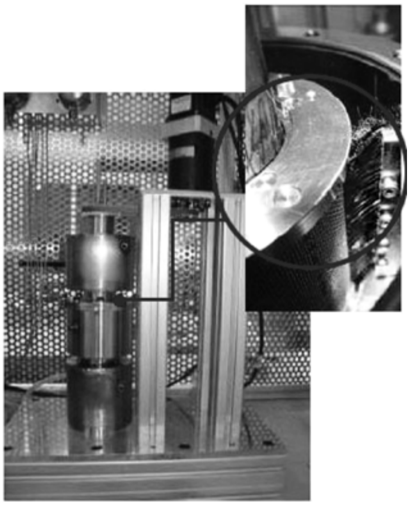

Figure 3 First version of 100kW rotating CLC reactor.

Department of Energy of USA specially pointed out that the chemical-looping combustion would be regarded as one of the advanced technologies of CO_2 capture in the future 10—15 years. Figure 4 illustrates the technology horizon for capture CO_2. It is clearly seen that chemical-looping combustion is listed as the most advanced technology. In the August of 2008, DOE of USA also announced to fund 3600 millions for the fifteenth research program of CO_2 capture, where the chemical-looping combustion as the first and foremost technology, is to be supported$^{1)}$. This project will be further developed on the basis of the integrated CLC combustion-gasification power system by ALSTOM. Its overall objective is to build industrial pilot facility to enable ALSTOM to design, construct, and demonstrate this advanced chemical-looping combustion system.

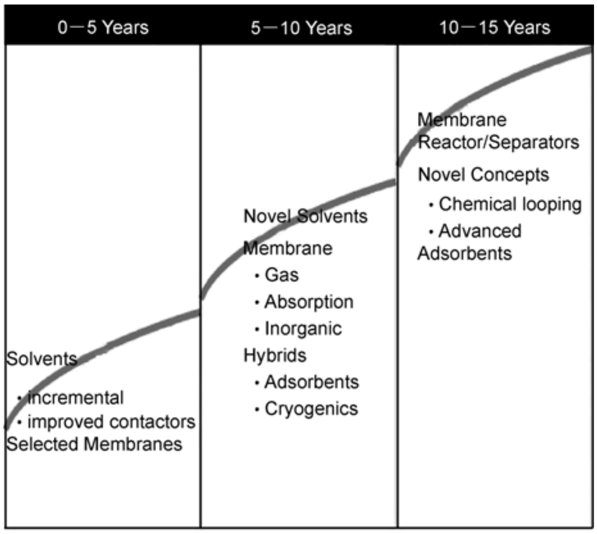

Figure 4 The development trend of CO_2 capture technology.

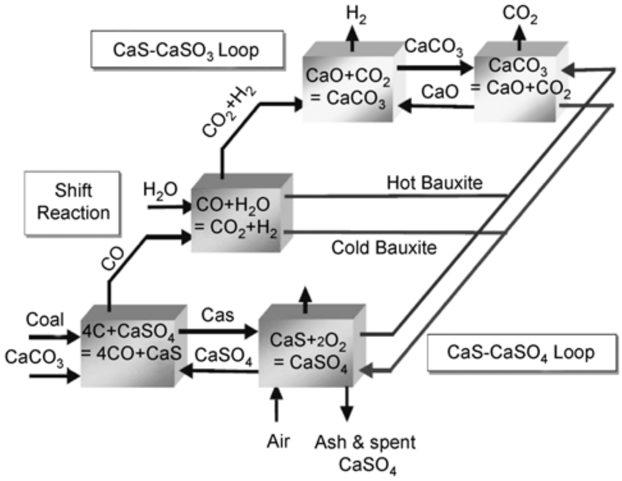

Figure 5 Schematic of the integrated CLC combustion-gasification developed by ALSTOM.

The diagram of the integrated CLC combustion-gasification developed by ALSTOM$^{2)}$ is shown in Figure 5. The calcium compounds are used to carry oxygen and heat between the various reaction loops. The first chemical loop uses CaS & $CaSO_4$ reactions to gasify the coal. With the addition of steam, this gas is converted to hydrogen and carbon dioxide. The carbon dioxide is then removed from the gas using another chemical loop based on CaO & $CaCO_3$. These compounds are then directed to another reactor where a "thermal" loop, using a bauxite heat transfer medium, drives off the carbon dioxide for use or sequestration. This system has been shown to have the potential to achieve near-zero CO_2 emissions, meet or beat IGCC efficiency, and cost less than \$800 per kilowatt without CO_2 capture and less than \$1000 per kilowatt including CO_2 capture for the world-wide power generation market. In order to avoid

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1) http://www.fossil.energy.gov/programs/sequestration/cslf/index.html

2) http://www.netl.doe.gov/publications/factsheets/project/Proj293.pdf

the carbon entering into the air reactor and the influence of ash on the system, measures should be taken to separate the oxygen carrier from the unburned carbon particles and ash. Chalmers University of Technology[8,9], Southeast University[10] and CANMET Energy Technology Centre[11] in Canada have done researches in this field.

At present, the combination of chemical-looping combustion and power generation is becoming an important direction to the synthesis of energy system compatible with environment, and is one of the advanced technologies of solving the greenhouse problems. In this paper, the object is to review the development of the integration of chemical-looping combustion and power generation from the mechanism of the energy release of the chemical-looping combustion (CLC), the oxygen material and reactor, and the system synthesis, to find out the difficulties of the current investigation, and finally, to make a prospect for this kind of new technology of CLC.

1 Mechanism of energy release of chemical-looping combustion

As well as known, the largest exergy destruction in thermal cycles takes place in the combustion process, instead of in the transformation of physical energy. Conventionally, lowering down the exergy destruction in combustion is mainly dependent on increasing the initial temperature (higher than 1400℃) of thermal cycle for the improvement of thermal efficiency. That is to say, this approach just considers raising the energy level of the energy acceptor, i.e. gas from the outlet of turbine. Nevertheless, this possibility is becoming smaller and smaller due to the limitation of technology of thermal engine and material. Hence, further efforts for the improvement of thermal efficiency should be directed to the innovative combustion process, and at the same time, should take a new approach of energy conversion. Chemical-looping combustion may be provided as a resolvable and practical way.

Unlike the direct combustion of fuel, chemical-looping combustion is capable of decomposing the simple and direct combustion of fuel into two successive reactions. In this way, chemical energy may be utilized step by step from energy level A_{ch1} to energy level A_{ch2}, as shown in Figure 6. Here, the energy level of A indicates the ratio of the exergy change to enthalpy change for a given energy conversion process[12]. A_{ch} refers to the energy level of chemical energy of fossil fuel, while A_{Th}, level of thermal energy, i.e. the energy level of high-temperature flue gas of the inlet gas turbine.

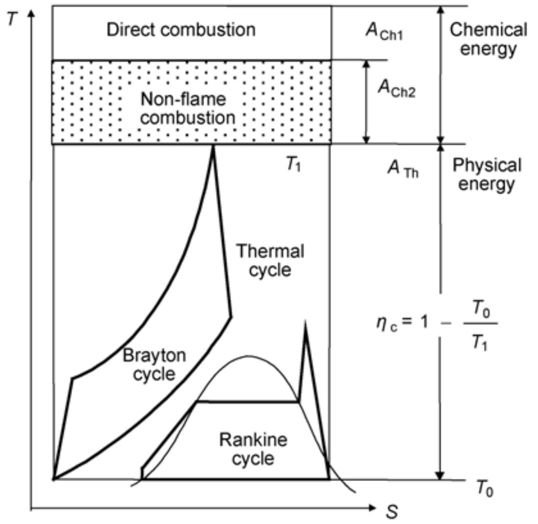

Figure 6 Schematic of mechanism of energy release of chemical-looping combustion.

In the chemical-looping combustion, the reduction of metal oxide makes the chemical energy of fossil fuel converted into the metal fuel. Since the energy level of metal fuel is lower than that of fossil fuel, the energy level of chemical energy is degraded from A_{ch1} to A_{ch2} in the chemical reaction. After that, as the metal fuel carries out the next oxidation reaction, the energy level of chemical energy (A_{ch2}) is converted into thermal energy A_{Th}. In this way, the energy-level difference between the chemical energy and the thermal energy is decreased from (A_{ch1}-A_{Th}) to (A_{ch2}-A_{Th}), compared with the direct combustion. In fact, the energy level from A_{ch1} to A_{ch2} as a “driving force”, is utilized to upgrade the energy level of the middle-and-low temperature heat. That is to say, this part of the chemical energy corresponding to energy level from A_{ch1} to A_{ch2} is firstly recovered by means of chemical reaction, and then the left chemical energy corresponding to energy level from A_{ch2} to A_{Th} is converted into thermal energy. Thus, the chemical energy of fossil fuel may be indirectly released through the two reactions, rather than the simple and direct combustion. In other words, the chemical-looping combustion can lead to the effective use of chemical energy prior to combustion of fuel, bringing about the decrease of irreversibility in the chemical energy of fuel converted into thermal energy.

Based on our research on the cascade utilization of chemical energy[13], the mechanism of energy release of chemical-looping combustion is disclosed.

1.1 Increase of thermal exergy of energy system

For comparison, the temperature of exothermic reaction in chemical-looping combustion is set as the same as in the direct combustion, i.e. there is the identical energy level of thermal exergy of combustion products (η_1). For different kinds of combustion processes, their thermal exergies are, respectively, taken into account:

Thermal exergy of the direct combustion $\Delta E_{\mathrm{th}1}$:

$$\Delta E_{\mathrm{th}1} = \Delta H_1 \eta_1 , \tag{3}$$

where, the term of ΔH_1 is the reaction enthalpy of direct combustion.

For the chemical-looping combustion, if the thermal exergy $\Delta E_{\mathrm{th}2}$ ($\Delta E_{\mathrm{th}2}=\Delta H_2\eta_2$) provided for the endothermic reaction is considered, then the thermal exergy of the chemical-looping combustion $\Delta E_{\mathrm{th}3}$:

$$\Delta E_{\mathrm{th}3} = \Delta H_3 \eta_1 - \Delta H_2 \eta_2 . \tag{4}$$

The terms of ΔH_3 and ΔH_2 denote, respectively, the reaction enthalpies of exothermic oxidation reaction and endothermic reaction in the chemical-looping combustion or the indirect combustion. The item of η_2 stands for the energy level of thermal energy provided for the endothermic reaction. Since endothermic reaction increases the value of enthalpy of the reaction productions, according to energy balance, we have $\Delta H_3 = \Delta H_1 + \Delta H_2$. Thus, expression of (4) may be rewritten as:

$$\Delta E_{\mathrm{th}3} = \Delta H_1 \eta_1 + \Delta H_2 (\eta_1 - \eta_2) . \tag{5}$$

By subtracting Eq. (3) from Eq. (5), we have

$$\Delta E_{\mathrm{th}} = \Delta E_{\mathrm{th}3} - \Delta E_{\mathrm{th}1} = \Delta H_2 (\eta_1 - \eta_2) . \tag{6}$$

In case of $\eta_1 > \eta_2$, ΔE_{th} is larger than zero; while in case of $\eta_1 \leqslant \eta_2$, ΔE_{th} is smaller or equal to zero. The relation of $\Delta E_{\mathrm{th}} > 0$ means the increase in thermal exergy of energy system with chemical-looping combustion, compared with the thermal cycle with direct combustion. This benefit of thermal exergy is equal to $\Delta H_2(\eta_1 - \eta_2)$.

1.2 Interaction between increase of thermal exergy and decrease of exergy destruction of combustion reaction

According to exergy balance, fuel exergy ΔE_1 in direct combustion is given as,

$$\Delta E_1 = \Delta EXL_1 + \Delta E_{T1} , \tag{7}$$

where, the term of ΔEXL_1 refers to the exergy destruction in the direct combustion, and ΔE_{T1} denotes the thermal exergy released from the combustion products.

In chemical-looping combustion, the exergy balance for NiO reduction reaction and Ni oxidation reaction are separately obtained:

$$\Delta E_1 + \Delta E_{T2} = \Delta EXL_2 + \Delta E_3 , \tag{8}$$

$$\Delta E_3 = \Delta EXL_3 + \Delta E_{T3} . \tag{9}$$

The term of ΔE_{T2} on the left-hand side of Eq. (8) stands for the thermal exergy provided for the endothermic reaction. On the right-hand side of Eq. (8), the term of ΔEXL_2 means the exergy destruction in the endothermic reaction, and ΔE_3 represents the exergy of products of Ni. The term of ΔEXL_3 in Eq, (9) refers to the exergy destruction in the oxidation reaction of nickel, and the term of ΔE_{T3} denotes the thermal exergy of the products. Inserting Eq, (9) into Eq, (8) yields

$$\Delta E_1 + \Delta E_{T2} = \Delta EXL_2 + \Delta EXL_3 + \Delta E_{T3} . \tag{10}$$

Based on our research [13], the exergy of fuel ΔE_{f} is expressed as: $\Delta E_{\mathrm{f}} = \Delta G(1-\eta_1)+\Delta H_{\mathrm{f}}\eta_1$, then the exergy of fuel ΔE_1 in the direct combustion and the exergy (ΔE_3) of products of Ni in the chemical-looping combustion are, respectively, given as:

$$\Delta E_1 = \Delta G_1 (1-\eta_1) + \Delta H_1 \eta_1 , \tag{11}$$

$$\Delta E_3 = \Delta G_3 (1-\eta_1) + \Delta H_3 \eta_1 . \tag{12}$$

The terms of $\Delta H_1\eta_1$ and $\Delta H_3\eta_1$ are, respectively, equivalent to the thermal exergies of combustion products ΔE_{T1} and ΔE_{T3}, i.e. $\Delta H_1\eta_1=\Delta E_{T1}$ and $\Delta H_3\eta_1=\Delta E_{T3}$. The terms of ΔG_1 and ΔG_3 refer to, respectively, Gibbs free energy changes in the oxidation reaction of nickel and syngas combustion. By introducing Eqs. (11) and (12) into Eqs. (7) and (9), respectively, we have

$$\Delta G_1 (1-\eta_1) = \Delta EXL_1 , \tag{13}$$

$$\Delta G_3 (1-\eta_1) = \Delta EXL_3 . \tag{14}$$

Similarly, the exergy destruction in the endothermic reaction is $\Delta EXL_2=\Delta G_2\ (1-\eta_2)$, where ΔG_2 stands for Gibbs free energy change in the endothermic reaction. Thus, Eq. (10) becomes

$$\begin{aligned} &\Delta G_1 (1-\eta_1) + \Delta H_1 \eta_1 + \Delta E_{T2} \\ &= \Delta G_2 (1-\eta_2) + \Delta G_3 (1-\eta_1) + \Delta H_3 \eta_1 . \end{aligned} \tag{15}$$

Since $\Delta E_{T2} = \Delta H_2\eta_2$ and $\Delta H_3=\Delta H_1+\Delta H_2$, then Eq. (15) may be reduced to

$$\Delta H_2 (\eta_1 - \eta_2) = (\Delta G_1 - \Delta G_3)(1-\eta_1) - \Delta G_2 (1-\eta_2) . \tag{16}$$

Based on our research[13], the energy level of Gibbs free energy (B) in the chemical reaction is defined as: $B=\Delta G/$

ΔH and Equation (6) $\Delta E_{\mathrm{th}} = \Delta H_2$ $(\eta_1 - \eta_2)$, we have E. (17)

$$\Delta E_{\mathrm{th}} = \Delta H_1(B_1 - B_3)(1-\eta_1) \\ -\Delta H_2 B_2(1-\eta_2) - \Delta H_2 B_3(1-\eta_1)\,. \tag{17}$$

Thus, Eq. (17) discloses the interactions among the increase of the thermal exergy of energy system, the energy level B of Gibbs free energy of combustion reaction and exergy destruction. On the right-hand side of Eq. (17), B_1 refers to the energy level of Gibbs free energy ΔG_1 in the direct combustion of fuel, B_3 denotes the energy level of Gibbs free energy ΔG_3 in the exothermic oxidation reaction of chemical-looping combustion or indirect combustion, and B_2 stands for the energy level of Gibbs free energy ΔG_2 in endothermic reaction. Thus, the term of $(B_1 – B_3)$ indicates the effective utilization of energy level of chemical energy in the chemical- looping combustion or indirect combustion, with comparison of the direct combustion, and ΔH_1 $(B_1 – B_3)$ $(1 – \eta_1)$ refers to the part of the utilized chemical exergy where $\Delta H_1 B_1$ $(1 – \eta_1)$ denotes the destruction of chemical exergy in the direct combustion. In addition, B_2 $(1 – \eta_2)$ refers to the degradation of energy level of Gibbs free energy in the endothermic reaction, while B_3 $(1 – \eta_1)$ represents one of the exothermic oxidation reactions of nickel and syngas combustion, and accordingly, $\Delta H_2 B_3$ $(1 – \eta_1)$ and $\Delta H_2 B_2$ $(1 – \eta_2)$ stand for, respectively, their exergy destructions corresponding to energy conversion of ΔH_2.

From Eq. (17), we may observe that the increase in thermal exergy of energy system with the chemical-looping combustion is closely related to the effective utilization of energy level of Gibbs free energy from B_1 to B_3, (i.e. the difference between B_1 and B_3) according to the energy level grade, in which the released chemcial energy of fossil fuel may be gradually converted and the irreversibility of the combustion is decreased Thus, this kind of energy conversion process may provide a new approach of the cascade utilzation of chemical energy for power generation system.

At present, stage achievement has been acquired in the research of energy release mechanism of the chemical-looping combustion. However, the interactions between the cascade utilization of chemcial energy and the decrease of energy penalty of CO_2 separtion has been not yet disclosed. This research is difficult, because relationships among the energy conversion, material production and CO_2 separation during the combustion process are more complex, involving the cross of thermodynamics and physical chemistry. However, it has an important theoretical value in the building of theoretical framework of greenhouse gas control.

2 Oxygen carrier development and reactor design

2.1 Oxygen carrier development

The development of a suitable looping material, with high reactivity, strong selectivity and high ability of regeneration in the cyclic reduction and oxidation, is the vital technology of a thermal cycle with chemical-looping combustion. The bulk of oxygen carrier research in the literature focuses on Ni based, Cu based and Fe based materials. In early research, Ni based oxygen carriers were studied by many researchers for their high reduction and oxidation rates and conversions, good regenerability and so on. The major contributors include Tokyo Institute of Technology in Japan[14,15], Purdue University in America[16] and Politecnico di Milano in Italy[17]. The metal Ni, however, is too expensive. Besides, it catalyzes carbon formation. Cu based oxygen carriers have better oxygen capacity. They are less expensive and can not catalyze cracking of CH_4 which causes carbon formation. CuO/Cu oxygen carriers have good reactivity. The carriers prepared by impregnation exhibited excellent regenerability and carriers prepared by co-precipitation can bear higher temperature than other Cu based oxygen carriers. Despite these, Cu based oxygen carriers are prone to agglomerate under high temperature, which limits their application in high temperature reactions[18–20]. Fe based oxygen carries are relatively inexpensive and environmentally safe, but their reactivity is worse than the Ni based ones, their reduction and oxidation rates are much lower[21,22]. Oxygen carriers of metal oxides like Ni based, Cu based, Co based and Mn based carriers will inevitably have some leakage to environment and become second pollution sources, so $CaSO_4$ has been considered to be a new type of oxygen carries by some researchers, which is much more cheaper and environmentally friendly, and Huazhong University of Science and Technology, Southeast University and CANMET Energy Technology Centre in Canada have done researches in this field[11,23,24].

To promote the commercialization process of chemical-looping combustion, the economy of oxygen carriers is becoming more and more important. However, the cost of synthetic oxygen carriers is too high. In addition, the lifetime of these oxygen carriers in a CLC-system with solid fuels may be restricted by deactivation caused by ash or by loss of material of the ash when separated from the oxygen carriers. Researchers have tried to use natural minerals like ilmenite and perovskite as cyclic materials[25,26]. The ilmenite has the advantages of excellent mechanical strength, low attrition rate, moderate reduction and oxidation rates and high oxygen capacity. When compared with $Fe_2O_3/MgAl_2O_4$, using ilmenite can reduce by a third of the amount of oxygen carrier. Carbon formation will not occur during the long defluidization period. It is found that ilmenite is an inexpensive oxygen carrier, and the price of ilmenite is about 100 times lower than that of Ni based oxygen carrier. This can substantially relax the requirements of the oxygen carrier lifetime in the case of that ash has effect on the performance of the cyclic material.

We have done many researches on developing oxygen carriers, and prepared some oxygen carriers of composite metal oxide by using NiO, Fe_2O_3, CuO, CoO, MnO etc. as the main oxygen carrier and Al_2O_3, SiO_2, YSZ, ZrO_2, MgO, TiO_2 etc. as additive. Among these oxygen carriers, the development of $NiO/NiAl_2O_4$ and CoO-NiO/YSZ[15,27] make a foundation for the future research work[28].

When using Al_2O_3 as additive material and NiO as reactant, a compound of the spinal type of $NiAl_2O_4$ is formed, and it can reduce the effective component content and the reduction conversion rate. It is important that $NiAl_2O_4$ is stable below a temperature of 1173 K. Hence, by making use of this feature, we have synthesized a looping material of $NiO/NiAl_2O_4$. In Figure 7 the reactivity of this new material is compared with that of the other two materials. It is clear that both reduction and oxidation rates of this new material are much higher compared with that of NiO/YSZ. In particular, both reactions can be completely performed. Another advantage is that the material cost of $NiAl_2O_4$ is much lower than that of YSZ, nearly 20% of YSZ.

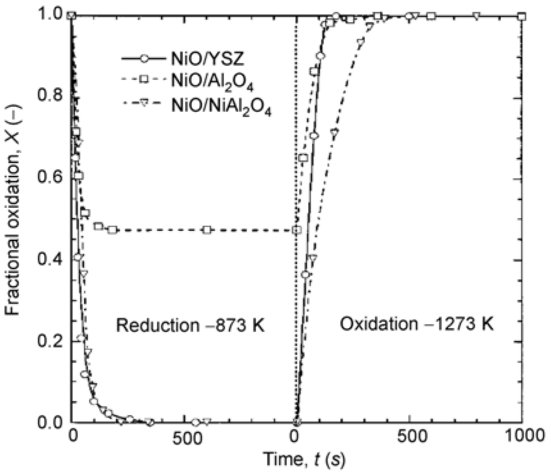

Figure 7 Effect of binder on reactivity.

Furthermore, when Ni based oxygen carriers react with carbonaceous fuel, fuel cracking will cause carbon deposition, which affects the regenerability of oxygen carriers. To avoid the carbon deposition, CH_4 was saturated at a ratio of H_2O/CH_4= 2.0[15,29]. The addition of water vapor may cause the steam reforming and shift reaction $CH_4 + H_2O=CO + 3H_2$, $CO + H_2O= CO_2 + H_2$, and no carbon deposition was found.

In the experiment of carbon deposition behavior for particles of NiO/YSZ and $NiO/NiAl_2O_4$ (Figure 8), we found out that, before saturation, the weights of particles were sharply increased due to carbon deposition after 200s. However, it was found that $NiO/NiAl_2O_4$ had no weight increase after saturation of fuel. It indicated that carbon deposition can be apparently reduced by addition of water into CH_4. The similar phenomena and conclusion are also obtained by other researchers[16].

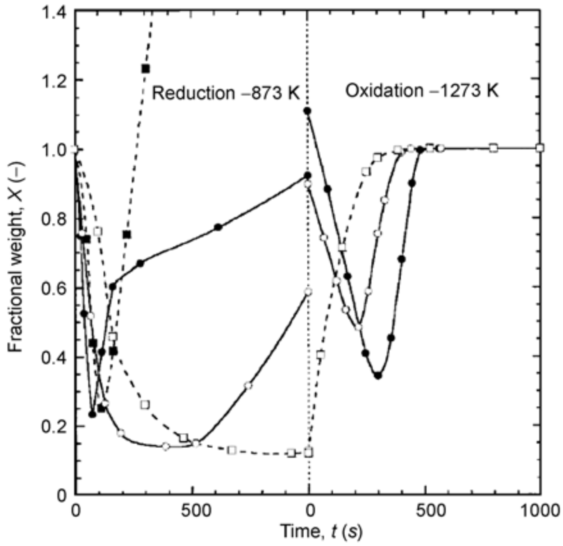

Figure 8 Effect of a double oxide particle on carbon deposition. Key:(—●—)NiO/YSZ(CH_4);(—○—)NiO/YSZ(H_2O/CH_4=2.0);(--■--)$NiO/NiAl_2O_4$(CH_4);(--□--)$NiO/NiAl_2O_4$(H_2O/CH_4=2.0)

Furthermore, by synergetic combination of nickel oxide with cobalt oxide, a new looping material has been synthesized by use of a double metal oxide and by addition of YSZ. This new looping material of CoO-NiO/YSZ had an excellent performance in high reactivity, complete avoidance of carbon deposition, and good repeatability. Figure 9 illustrates the cross-sectional

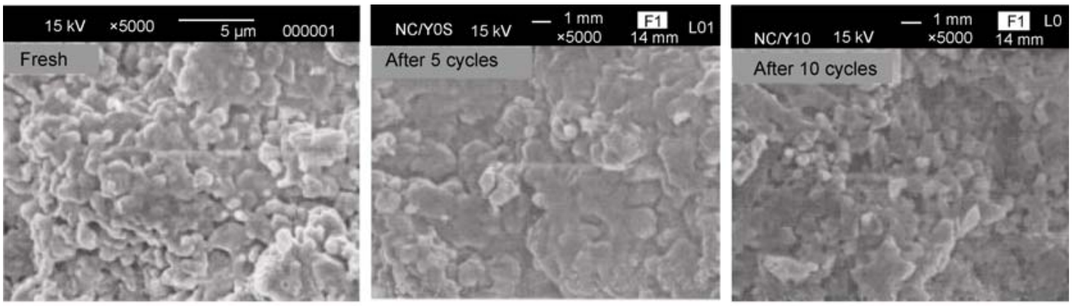

Figure 9 Cross-sectional photos of CoO-NiO/YSZ in the cyclic reaction.

photos of CoO-NiO/YSZ particles. The microstructure after the 10th cycle was similar to that of the fresh structure with grains 0.5—2.0 μm in diameter, which indicated that CoO-NiO/YSZ was relatively stable in the course of cyclic reactions, compared with those observed from the single metal oxides. The successful preparation of CoO-NiO/YSZ leads to a new direction of oxygen carrier research.

At present, most researches on oxygen carrier are still by experiment, and are mainly based on gas fuel. It is important for researchers to prepare suitable oxygen carrier for solid fuel, optimize the theoretical model and develop cheap, environment-friendly oxygen carriers in the future work.

3.2 Chemical-looping combustion reactor

Chemical-looping combustion system requires perfect contact between gas and solid oxygen carriers as well as a significant flow of solid material between the reactors. The gas leakage between the reactors must be minimized to prevent the carbon dioxide from being diluted by nitrogen, or to prevent carbon dioxide from leaking into the air reactor decreasing the efficiency of carbon dioxide capture. The research on chemical-looping combustion reactor has passed the period of fixed bed reactor and the period of fluidized bed reactor. In order to fulfill the engineering requirements of chemical-looping combustion reactors, designs of small-scale fluidized bed reactor and interconnected fluidized bed reactor have been proposed one after one since 2001, and prototypes for chemical-looping combustion have been designed, built and run. The interconnected fluidized bed reactor, designed by professor Anders Lyngfelt et al.[8,9] of Chalmers University of Technology, is considered to be the most ideal reactor at present (Figure 10).

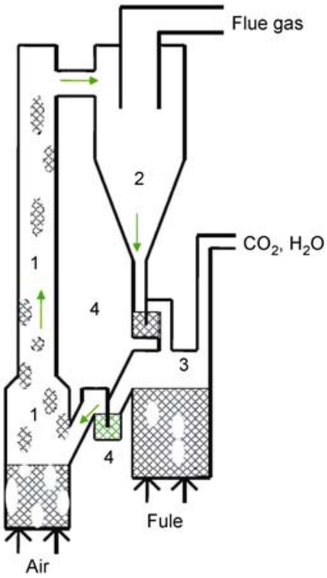

Figure 10 Layout of chemical-looping combustion process, with two interconnected fluidized beds. 1) air reactor; 2) cyclone; 3) fuel reactor.

The circulating system is composed of three parts: a high-velocity riser (1), a cyclone (2) and a low-velocity bubbling fluidized bed (3). In the air reactor, or the riser, oxygen is transferred from the combustion air to the oxygen carrier. In the low-velocity fluidized bed, or the fuel reactor, oxygen is transferred from the oxygen carrier to the fuel. The particles carried away from the riser are recovered by the cyclone and led to the fuel reactor. From the fuel reactor the particles are returned to the air reactor by means of gravity. Lyngfelt et al. gave the key design parameters of this reactor, and established the relations between these parameters and the cyclic characteristics. They investigated the gas leakage in a scaled cold model[30]. A typical leakage from the fuel reactor was 2%, i.e. a CO_2 capture efficiency of 98%. No leakage was detected from the cyclone to the fuel reactor. A typical leakage from the pot-seal into the fuel reactor was 6%, which would give a dilution of the CO_2 produced by approximately 6% air. However, this gas leakage can be avoided by using steam, instead of air, to fluidize the whole, or part of, the pot-seal.

Several CLC prototypes have been built, and performance tests of oxygen carriers have been made on them. A 10 kW_{th} prototype for chemical-looping combustion was built and run with nickel-based oxygen carrier particles by Lyngfelt[31]. Abad et al. studied the reactive characteristics of $NiO/MgAl_2O_4$, Mn_3O_4/Mg- ZrO_2 in a continuously operated laboratory reactor system for chemical-looping combustion with two interconnected fluidized beds[32]. Diego et al. of C.S.I.C in Spain also successfully built a $10kW_{th}$ CLC prototype[33]. To enable CLC technology as a competitive option for large-scale power generation with CO_2 capture, SINTEF and NTNU developed a 100 kW_{th} CLC rotating wheel reactor.

Most of the researches on CLC have been focusing on gaseous fuels. Because of low costs and abundance of solid fuels in the world, it seems worthwhile to adapt the process to solid fuel CLC. Figure 11 illustrates a 10 kW_{th} chemical-looping combustor for solid fuels designed by Chalmers University of Technology[34]. The design chosen for the 10 kW_{th} pilot using solid fuel is rather similar to the existing gas powered 10 kW_{th} constructed and operated at Chalmers, but important modifications in the fuel reactor chamber and the inclusion of an additional solids recirculation loop were made to adapt the system for solid fuels. Tests were made on this combustor with a South African coal and a petroleum coke as the solid fuels respectively and the oxygen carrier ilmenite[34–36]. The actual CO_2 capture ranged between 82.5% and 96% in the South African coal test. The CO_2 capture ranged from 60 to 75% in the petroleum coke test which was lower than that for the previous tests with a South African coal due to a less reactive fuel. Although there have been significant practical problems associated, mainly with “external” functions such as fuel feeding and gas analysis, it can be concluded that the testing gives proof of the concept for chemical-looping combustion of solid fuels.

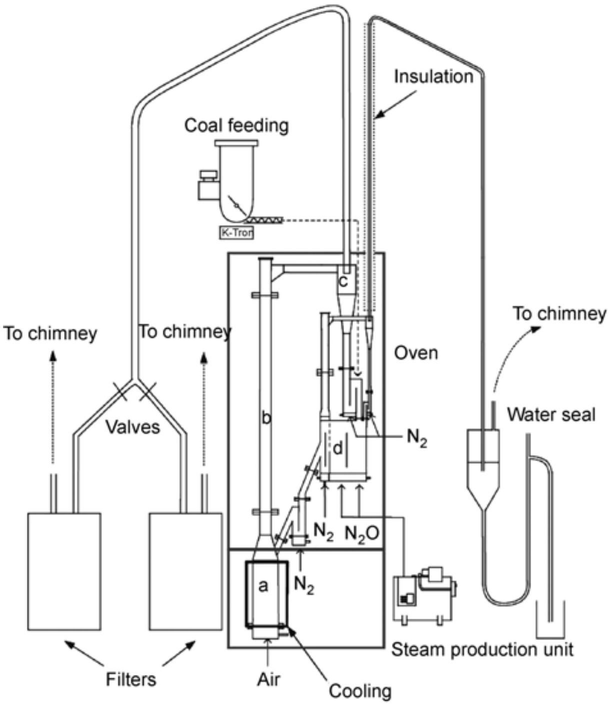

Figure 11 The pilot system of chemical-looping combustor for solid fuels: (a) Air reactor; (b) riser; (c) air reactor cyclone; and (d) fuel reactor.

Jonghwun Jung of Argonne National Laboratory and Isaac K. Gamwo of United States Department of Energy[37] developed the reaction kinetics model of the fuel reactor and implemented the kinetic model into a multiphase hydrodynamic model, MFIX. Simulated fuel reactor flows revealed high weight fraction of unburned methane fuel in the flue gas along with CO_2 and H_2O. Computational results from the simulation showed low fuel conversion rate partially due to fast, large bubbles rising through the reactor. To decrease the unburned methane fuel in the flue gas, the nano-size metal oxygen carrier might be a preferred candidate as it does not generate large bubbles and hence increases the conversion of fuel gas in the reactor.

Since chemical-looping combustion requires strictly on heat transfer, reaction rate, conversion rate of reaction process, and air tightness of reactor, research on reactor is still a difficult point in the development of CLC key technology. The problems, that how to low the pressure reduction, reduce the abrasion of oxygen carrier, avoid the gas leakage, are urgent to be solved. What’s more, research on theoretical model of reactor has just started, and need to be optimized.

3 Energy system with inherent CO_2 separation by using CLC

In essence, the combination of chemical-looping combustion with thermal cycle has introduced a special field of the integrated energy system with a cross scientific fields between energy and environment. Unlike conventional power system, the CLC energy system is a kind of approach to control pollutant by integrating the thermodynamics and environment chemistry. Currently, the study on the synthesis of energy system with CLC mainly focuses on the saturated air gas turbine cycle by only using syngas or natural gas fueled chemical-looping. However, there are still several key science problems undisclosed for system synthesis. For example, the mismatch of the energy levels between the reaction heat provided and the thermal energy utilized in the thermal cycle has not been paid attention to. Consequently, the combustion heat is usually applied to driving the reduction reaction of CLC. In this way, a wrong conclusion that the thermodynamic performance of chemical-looping combustion system is not superior to that of the conventional combined cycle is drawn. In addition, the energy conversion process of the chemical-looping combustion is simply considered as the CO_2 separation without extra energy penalty. However, the system synthesis has not been intensively and rationally investigated and disclosed from the viewpoint of the cascade utilization of chemical energy. Recently, from the viewpoint of the energy level, we also proposed the following chemical-looping combustion systems based on the previous researches.

3.1 Integrated coal-gasification CLC system

Ishida and Jin[38,39] found out a phenomenon that the reactivity of NiO with coal gas is much higher than that with natural gas (CH_4) in chemical-looping combustion, when adopting CH_4 and coal gas as fuel and NiO/$NiAl_2O_4$ as solid material, as shown in Figure 12. This is mainly due to the fact that the reduction of NiO with coal gas (CO and H_2) is a strongly exothermic reaction, and the reduction with CH_4 (natural gas) is an endothermic one and has less force to drive this reaction. This is completely different from the traditional combustion in which natural gas is considered as an ideal fuel. In addition, we also observed that there is no damage to the samples of solid materials, after more than 10 cycles of reduction and oxidation. This means that coal gas fueled chemical-looping combustion has high reactivity, avoidance of carbon deposition and regenerability. These results support the idea that the coal gas fueled chemical-looping combustion may lead to a breakthrough in combustion process, and open up a new direction for clean-coal technology.

From the former experimental results, we proposed a new integrated gasification combined cycle by applying the ideas of chemical-looping combustion and saturation of air (IGCLSA)[40], shown in Figure 13.

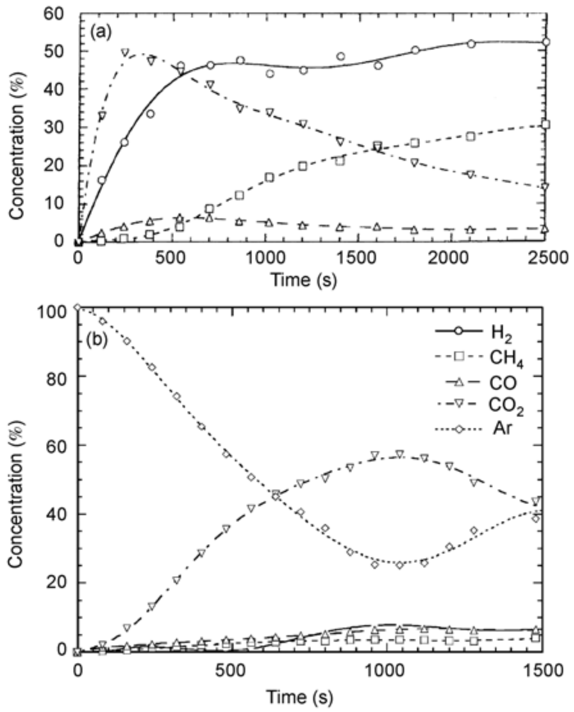

Figure 12 (a) Gas concentration and solid conversion during reduction. —O—H_2, --□--CH_4, —Δ—CO, —▽—CO_2, NiO/$NiAl_2O_4$, CH_4=33%, H_2O=67%, F = 300 mL/min, P = 1 ata, T = 973 K; (b) Variation of gas concentration during reduction by coal gas. CO=40%, H_2=20%, H_2O=20%, Ar=10%, CO_2=10%, NiO/$NiAl_2O_4$, F = 500 mL/min, P = 1 ata, T = 973 K.

The system mainly consisted of three main parts, coal gasification and purification unit, chemical-looping combustion unit and thermal cycle unit with saturated air. Purified coal gas mainly composed of H_2 and CO entered into the chemical-looping combustor and reacted with metal oxides: $H_2+CO+2NiO\rightarrow H_2O+CO_2+2Ni$. In the fuel reactor, products of H_2O and CO_2 were discharged from the upper part, and metal Ni exiting from the lower part entered into the air reactor and was oxidized into NiO by air, $Ni+0.5O_2\rightarrow NiO$. As strongly exothermic process existed, the temperature of gas increased sharply. Energy level of the oxidation process of Ni was lower than that of direct combustion process, which provided the potential to reduce the energy level difference during the reaction process. Thermal performance analysis indicated that thermal efficiency of IGCLSA could reach 51.3%, net power output was 232.4 kJ/mol-C, system efficiency was 5%—10% higher compared with conventional IGCC, and the generation of CO_2 per kWh electricity can be significantly decreased from 0.52 kgCO_2/kWh to 0.36 kgCO_2/kWh. Considering the current CO_2 recovery price 50\$/t-CO_2, for a 300MW IGCLSA system with 6000h operation time per year,

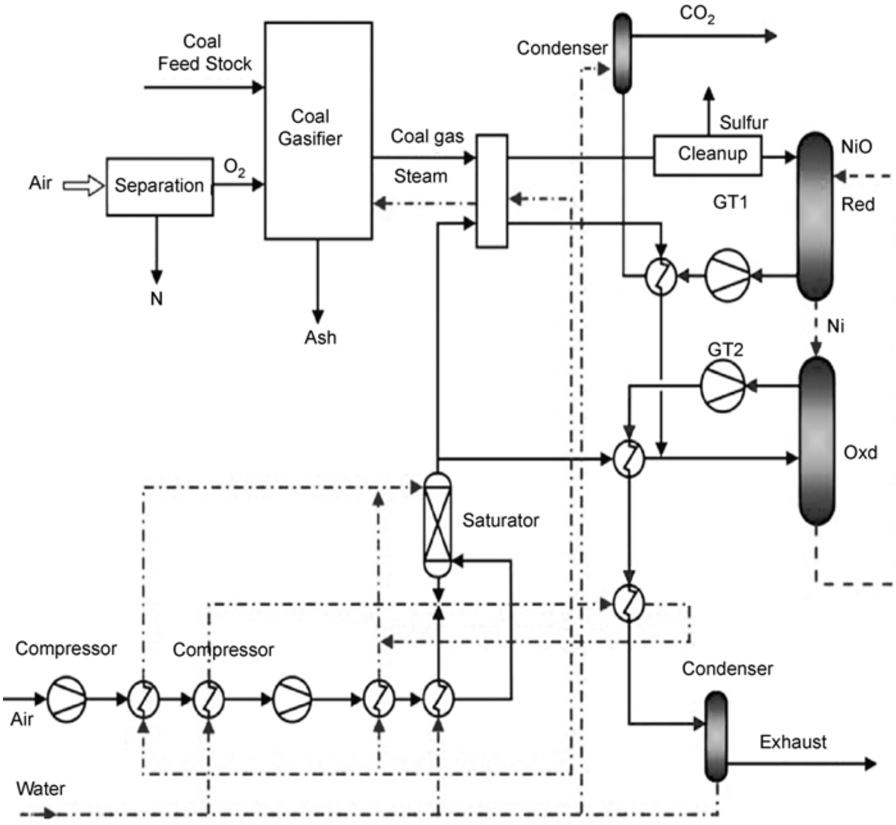

Figure 13 A process flow diagram for IGCLSA.

10.08 million RMB of CO_2 capture cost can be saved.

3.2 A novel gas turbine cycle with hydrogen-fueled chemical-looping combustion

H_2/O_2 gas turbine cycle is a special thermal cycle. There are no CO_2 capture and separation problems, for hydrogen is oxidized into H_2O after combustion. Therefore, Japan and America have paid much attention to it. However, H_2/O_2 gas turbine cycle has two fatal defects. First, from the exergy principle, since the heat exchange for steam generation is shifted into the combustor, it results in such significant energy level degradation from extremely high temperature by hydrogen combustion (>2500℃) to very low temperature for water evaporation (<350℃). The energy level degradation for steam generation in this cycle is much worse than that of the case using the heat recovery steam generator (HRSG) from medium temperature (650℃) to low temperature (<350℃) in a combined cycle. Another fatal defect in this cycle is the power consumption for producing pure oxygen before H_2/O_2 combustion, which causes an energy penalty of 11.5 percentage efficiency. To solve these problems, we proposed a novel gas turbine cycle with hydrogen-fueled chemical-looping combustion, shown in Figure 14[41].

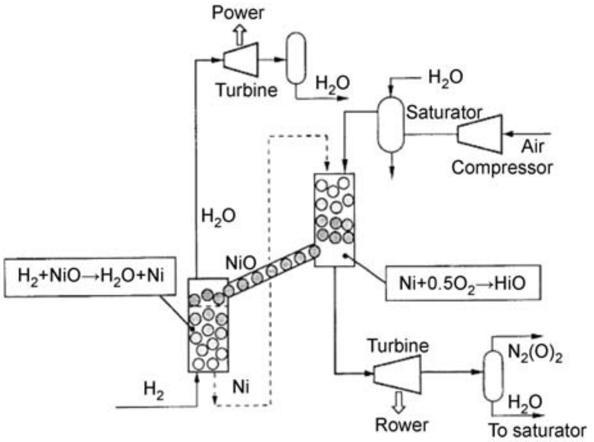

Figure 14 The concept diagram of H_2-fueled gas turbine cycle with chemical-looping combustion.

The hydrogen-fueled chemical-looping combustion consisted of two successive reactions: hydrogen with metal oxide (reduction) and the resulting metal with air (oxidation). The hydrogen fuel first reacted with the solid NiO in a reduction reactor, producing solid Ni and steam. In the next reactor, i.e. the oxidation reactor, the air saturated at an elevated pressure reacted with the solid Ni produced by the former reactor, yielding NiO and high-temperature flue gas by strongly exothermic oxidation. Finally, the gases exiting from both reactors could be used as the working fluid to generate power in turbines. In the new gas turbine cycle employing hydrogen-fueled chemical-looping combustion, the exergy losses in combustion and power consumption were much lower than those in the H_2/O_2 combined cycle. As a result, thermal efficiency in this new cycle with current-technology gas turbine (turbine inlet temperature of 1200℃) could be as high as 63.5%, increased by at least 12 percentage compared with that of the H_2/O_2 combined cycle (1350℃).

3.3 Solar hybridization power plant integrating methanol-fueled chemical looping combustion

Hybridizing fossil fuel energy and solar energy is more attractive in the application of solar thermal power plant. This hybridization is the endothermic processes, where fossil fuels are used exclusively as chemical reactants and solar thermal energy as a heat source for driving endothermic transformations. On the one hand, it can allow the conversion of solar energy into chemical energy for storage and allow solar energy to be used in combined cycles to generate electricity with effective conversion of solar energy to electric energy. On the other hand, fossil fuel can be converted into cleaner fuels such as syngas before combustion for continuous use. However, most reported researches are about the utilization of the concentrated solar thermal energy at the temperature above 1000℃ for driving steam reforming of methane/coal gasification. There remains two issues, namely the concentrator with higher concentration ratio still suffers from the expensive investment, and the conversion and release of the chemical energy of fossil fuel is still through the direct combustion.

In addition, one of the most promising options for substitution of fossil fuels appears to be the wide use of methanol. It can be produced from primary fuels such as natural gas, coal, biomass, etc., and transported and fed into many energy conversion systems. The crucial issue for the development of the wide application of methanol fuel is how we can devise new kinds of methanol-fueled power plants not only with higher thermal efficiency but also lower emission of greenhouse gas and effective recovery of CO_2.

In order to simultaneously resolve the difficulties of low solar-to-electric efficiency and the efficient utilization of chemical energy of fossil fuel, we proposed a methanol-fueled combined cycle synergistically integrating chemical-looping combustion and solar thermal energy at around 200℃[42], and made preliminarily experimental validation for the key process[43].

Figure 15 illustrates the detailed cycle configuration. Methanol-fueled chemical-looping combustion (CLC) consisted of two successive reactions: 1) solar driven Fe_2O_3 reduction with methanol fuel and 2) oxidation of the resulting FeO with air. The reduced solid product of the first reaction, FeO, was converted to Fe_2O_3 by oxidation in the second reaction. Here, Fe_2O_3 played the role of an oxygen carrier between the two reactions. The first reaction of Fe_2O_3 particles and methanol fuel was endothermic: $CH_3OH+3Fe_2O_3 \rightarrow 6FeO+2H_2O+CO_2$, and accomplished in the range of 100－150℃ at a pressure of 1bar, so the concentrated low-grade solar thermal energy was utilized to drive this reaction. The second reaction was an exothermic oxidation: $4FeO+3O_2 \rightarrow 2Fe_2O_3$, and released heat in the high-temperature region of 1000－1300℃. The high temperature exhaust gas from the oxidation reactor was fed to turbine GT1 to generate electricity. It was found that the instant net solar-to-electric efficiency of the proposed cycle could be ex-

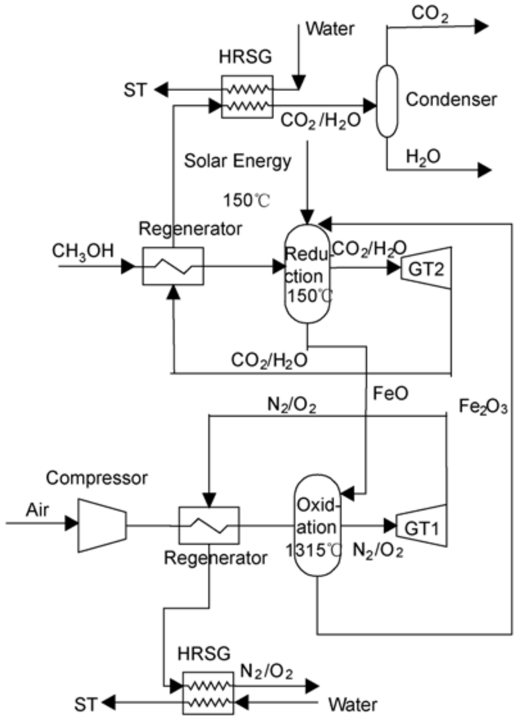

Figure 15 A process flow diagram for solar hybridization power plant integrating methanol-fueled chemical looping combustion.

pected to be 35%, superior to that of the state-of-art solar thermal power plant (15%) and competitive with the advanced solar steam reforming plant (30%).

In this cycle, solar thermal energy driven reduction of Fe_2O_3 by methanol fuel is the key process. The reactivity of methanol-fueled chemical-looping combustion was preliminarily examined by TGA. Figure 16 denotes the microstructures of a cross-section of the Fe_2O_3 particles observed by scanning electron microscopy before and after reaction. It was clearly seen that before reaction, the surface of the Fe_2O_3 particle was relatively smooth and compact. On the country, after reaction, there were large grains and pores in the particles. In addition, we might see that parts of the grains were broken down into smaller grains and agglomeration. These agglomerated grains might lead to the decrease in reaction rates. Therefore, it should avoid the breakdown and agglomerate of the larger particles during the reaction. Further research is being conducted.

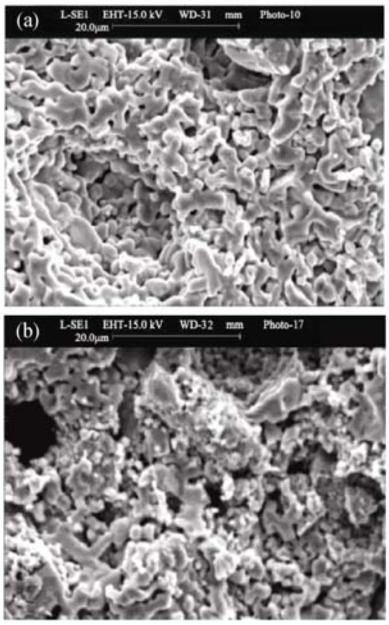

Figure 16 The microstructures of a cross-section of the Fe_2O_3 particles. (a) Before reaction; (b) after reaction.

In addition, we also proposed the novel gas turbine cycle hybridizing solar thermal energy with natural-gas fueled chemical-looping combustion[44]. This system can allow the concentrated solar thermal energy at around 1000℃ to be lowered down to 500℃, and provide a possibility of application of power system hybridizing solar energy with natural gas. Especially for some districts of China, such as Xin Jiang and Qing Hai, rich in solar energy and natural gas resources, the solar-hybrid gas turbine combined cycle with natural-gas fueled chemical-looping combustion can be applied not only to power generation, but also to chemical plants and production of clean fuels.

5 Conclusion

Exploring the novel energy system, integrating chemical-looping combustion and thermal cycle for CO_2 separation, is one of the main science issues on the cross fields between energy science and environment science. The breakthrough in these fields will generate an embranchment of burgeoning disciplines among energy, environment, and chemical industry. It will bring about a scientific and technological revolution in the next-generation energy-environment system.

This paper reviews the mechanism of the energy release of chemical-looping combustion, the development of oxygen carrier materials and reactors, and energy system synthesis. These researches have achieved a serial of important fruits. However, there still remains scientific issues to be explored. For example, the interactions between the cascade utilization of chemical energy and the decrease of energy penalty for CO_2 separation in the CLC, the influence of microstructure of oxygen carrier on the chemical reaction, the reactivity of CLC with liquid or solid fuel, and the universal design theory and methodology of fluidized bed reactor, etc., are not yet disclosed. In addition, the rational mechanism of the role of CLC in the improvement of thermodynamic performance and the principle of energy system synthesis with CLC are not explored. Especially, with the development of energy system by hybridizing with multi-energies, the chemical-looping combustion energy system will integrate the renewable energy and chemical industry of producing clean fuels, even crossing with the more broad fields. Therefore, it is urgent to build the theoretical framework of energy system with chemical-looping combustion. It is extremely important of the synthesis of energy system with greenhouse control.

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