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Chemical Looping Process - A Novel Technology for Inherent CO_2 Capture

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ABSTRACT

Chemical looping is a novel energy technology that undertakes inherent CO_2 capture and has better energy efficiency than existing CO_2 capture technologies. Metal oxides (also known as oxygen carriers) are applied for the chemical looping process in place of air to offer oxygen for fuel combustion, thus enhancing CO_2 purity in the effluent stream. This article introduces the major aspects of chemical looping technology, including the oxygen carrier, reactor and fuel. Fe-, Ni- and Cu-based metal oxides were found to be suitable oxygen carriers for the chemical looping process based on the evaluation indexes of oxygen capacity, cost, reactivity, and mechanical strength. The modification of oxygen carriers by supporting materials is the typical research regime for enhancing mechanical strength and reactivity. The reactor systems currently used for the chemical looping process include fluidized and moving bed reactors. Fluidized bed reactors are well developed for gaseous fuel combustion applications, while moving bed reactors operated with a counter-flow mode between the solid fuel and oxygen carriers would enhance combustion efficiency, and reduce the operating solid inventory of oxygen carriers. Gaseous fuels, including natural gas and syngas gasified from coal, could achieve complete fuel conversion and high CO_2 yield for different combinations of oxygen carrier and reactor system. Gasification of solid fuels, including coal, petroleum coke and biomass in the fuel reactor, is a critical step that might reduce overall combustion efficiency. To improve solid fuel combustion and CO_2 yield, modification of the reactor design or operational conditions are necessary for the combustion of solid fuels by a chemical looping process.

Keywords: Carbon dioxide; Chemical looping; Oxygen carrier; Fluidized bed reactor; Moving bed reactor.

DESCRIPTION OF CHEMICAL LOOPING PROCESS

Chemical looping is a concept using chemical intermediates to continuously react and regenerate for generating energy and/or desired chemicals. Howard Lane designed a fixed bed reactor for steam-iron process to generate H_2 in 1904 (Fan, 2010). In the steam-iron process, iron was the chemical intermediate that oxidized by steam to generate H_2, and was reduced by CO or H_2 to complete the chemical looping reaction scheme (Hurst, 1939; Hacker *et al.*, 2000). CO_2 generation for beverage industry had been employed chemical intermediates, such as CuO and Fe_2O_3, to be circulated between two fluidized bed reactors for generation of CO_2 and regeneration of chemical intermediates (Lewis and Gilliland, 1954).

Chemical looping was first introduced by Richter and Knoche (1983) for heat generation using metal oxides as chemical intermediates, and is considered a promising technology for efficient power generation as well as inherent CO_2 capture for possible carbon reuse or storage (Figureoa *et al.*, 2008). For chemical looping process, a fuel reactor and an air reactor are utilized for fuel combustion and heat generation, respectively, as illustrated in Fig. 1. Metal oxide (Me_xO_y) is reduced by carbonaceous fuel to generate CO_2 and/or H_2O in the fuel reactor as described as reaction (1). The reduced metal (Me_xO_{y-1}) is then oxidized to Me_xO_y by oxygen in the air reactor as described as reaction (2), which is an exothermic reaction that provides heat to external facilities.

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1} \quad (1)$$

$$2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y \quad (2)$$

For practical operation of chemical looping system, oxygen carrier particles are transported within and between the fuel reactor and the air reactor. Currently, fluidized bed and moving bed reactor systems are developed for the application of chemical looping process, depending on the

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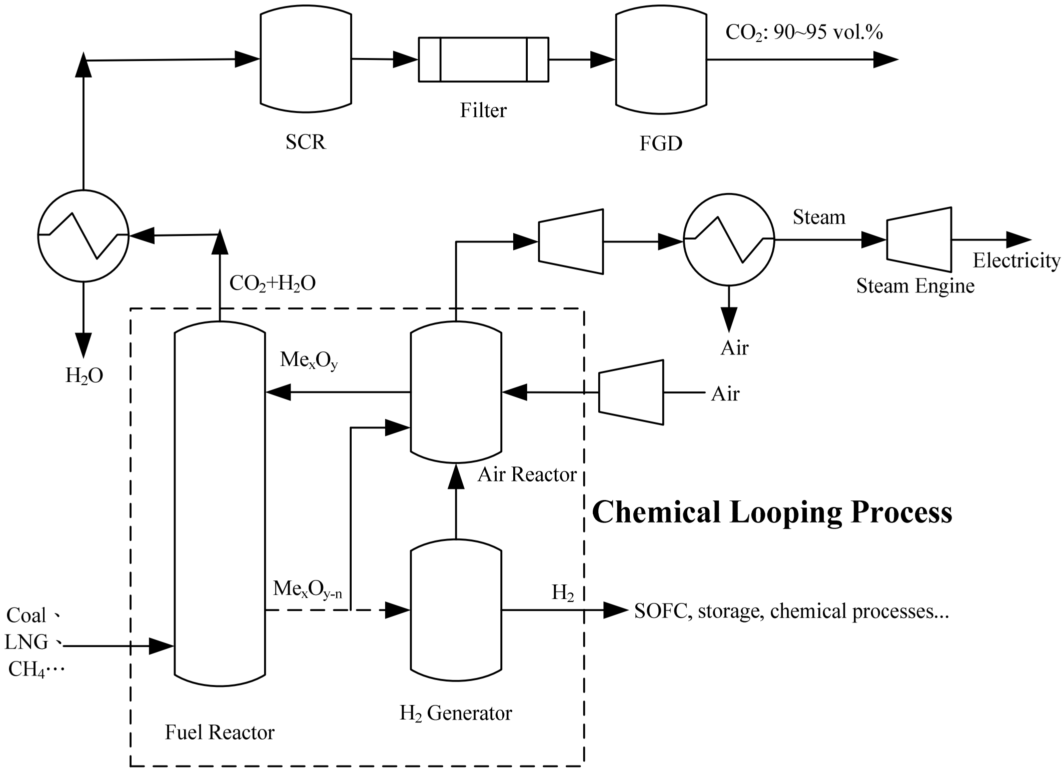

Fig. 1. Chemical looping process for power generation.

mode of transportation of oxygen carrier particles in the fuel reactor.

Development of chemical looping technology is extremely rapid in last decade while tests of pilot scale reactors for thousands hour operation were proceeded in many countries around the world with various fuels, such as syngas, methane, natural gas, coal, petroleum coke and biomass (Mattisson *et al.*, 2001; Johansson *et al.*, 2006; Leion *et al.*, 2009; Shen *et al.*, 2009a; Lyngfelt, 2011). The chemical looping reactors are suggested to substitute the conventional boilers for power generation, as illustrated in Fig. 1; high concentrations of CO_2 can be captured in the flue gas emitted from the fuel reactor while the air reactor is connected with steam engine for electricity generation. Besides, hydrogen can be an alternative product by oxidation of reduced oxygen carriers in the H_2 generator as illustrated in Fig. 1. The H_2 can be generated by employment of Fe-based oxygen carriers through chemical looping operation, and transported to external units, such as solid oxides fuel cell (SOFC), storage and chemical processes (Li and Fan, 2008). Efficiency of electricity generation for syngas (CO/H_2) combustion by chemical looping process was evaluated to be 43.2% (on LHV basis) (Xiang and Wang, 2008), much higher than those for pulverized coal power plants with amine absorption for CO_2 capture, estimated to be about 21 to 35% (Li and Fan, 2010).

The development of chemical looping technology can be divided by three categories, including oxygen carriers, reactors and fuels. The oxygen carrier is the core of chemical looping technology, the performance of reactivity, recyclability and mechanical strength is crucial for long-term and continuously operation in the chemical looping reactor system. In addition, cost of oxygen carrier is considered as one of the most important issues to commercialize chemical looping technology. Recently, low cost Fe-based oxygen carriers are trying to employ for solid fuel combustion; however, low reactivity of Fe-based oxygen carriers should be resolved through modification of oxygen carriers and retrofit of the reactor design to increase fuel conversion efficiency. Chemical looping combustion of gas fuels, such as syngas and natural gas have been widely validated to provide with high combustion efficiency by chemical looping process. However, for solid fuel combustion, gasification is a rate-limiting step in the fuel reactor to reduce the overall combustion efficiency. Therefore, how to improve the solid fuel combustion efficiency by enhancing gasification rate or prolonging residence time by reactor operation is a challenge to achieve solid fuel chemical looping combustion with high fuel conversion efficiency.

OXYGEN CARRIERS FOR CHEMICAL LOOPING PROCESS

Oxygen carriers applied for chemical looping process should provide excessive oxygen carrying capacity, high reaction rate, great mechanical strength, and long-term recyclability (Hossain and de Lasa, 2008). Ni-, Fe-, Cu-, Mn- and Co-based metal oxides are the typical materials to be employed as oxygen carrier for chemical looping process (Mattisson *et al.*, 2003). $CaSO_4$ was also used for transferring oxygen for methane combustion in fluidized bed reactors (Song *et al.*, 2009). However, sintering and attrition of these oxygen carriers during chemical looping operation are considered to be the main concerns to reduce their reactivity and recyclability. Therefore, the coupling of oxygen carriers with support materials, such as Al_2O_3, TiO_2, ZrO_2, $NiAl_2O_4$, MgO, SiO_2, $Y_2O_3 + ZrO_2$ (YSZ), sepiolite and $MgAl_2O_4$, is employed for improving the life of the oxygen carriers for long-term operation (Adanez *et al.*, 2004). Fabrication techniques of composite oxygen carriers with suitable particle size and mechanical strength include mechanical mixing, co-precipitation, dissolution, freeze-granulation, impregnation and spray drying (de Deigo *et al.*, 2005; Gayan *et al.*, 2008; Hossain and de Lasa, 2008).

The redox analysis by TGA is a typical preliminary procedure to evaluate the reactivity and recyclability of oxygen carriers employed for chemical looping process (Adanez *et al.*, 2004; Mattisson *et al.*, 2003; Li *et al.*, 2009). The degree of conversion for a specific oxygen carrier is the fraction of oxygen in the oxygen carrier that reduced by fuel, and defined by Eq. (3):

$$X_{OC} = \frac{m_o - m(t)}{m_o - m_r} \tag{3}$$

where m_o is the weight of fully oxidized oxygen carrier; m_r is the weight of fully reduced oxygen carrier; $m(t)$ is the weight of oxygen carrier at a specific operation time, t. For instance, TiO_2 supported Fe_2O_3 illustrated stable degree of conversion for 100 redox cycles conducted with 10% CO and 10% H_2 for reduction and air for oxidation processes at 900°C in TGA as shown in Fig. 2 (Liu, 2011). The preliminary test by TGA with stable reactivity for continuous redox cycling as illustrated in Fig. 2 can be selected to examine in a bench scale chemical looping reactor to assess its fuel conversion efficiency as well as degree of agglomeration after long-term operation.

For the application of oxygen carriers in chemical looping process, the partial pressure of CO_2 and H_2O should be as high as possible to approach 100% of CO_2 yield. Therefore, the analysis of equilibrium phase diagram between metal oxide and fuel is a feasible tool for selecting appropriate oxygen carriers. Gupta *et al.* (2007) analyzed the equilibrium phase diagrams of numerous Ni-, Cd-, Cu- Co-, Mn-, Sn- and Fe-based metal oxides as reacted with CO and H_2 that would be fully oxidized by these metal oxides. Cao and Pan (2006) compared the phase diagrams of metal oxides with regards to syngas indicated that Cu- and Fe-based metal oxides exhibit highest ratios of p_{CO2}/p_{CO} and p_{H2O}/p_{H2}, both are approximately 10^5. Hence, through the analysis of thermodynamic phase diagrams, high CO_2 yields can be achieved without additional separation unit by selecting proper metal oxides for chemical looping process operated at suitable temperatures.

The properties of Fe-, Ni-, Cu-, Mn- and Co-based oxygen carriers are listed in Table 1. The properties for selection of an oxygen carrier for chemical looping process are including oxygen capacity, cost, reactivity, conversion efficiency of fuel, melting point, mechanical strength and impacts on environment and health (Fan, 2010). Beside of these properties, the use of support materials for better performance on reactivity and mechanical strength are summarized in the last column of Table 1 for reference (Adanez *et al.*, 2012). Most Fe-based oxygen carriers demonstrate higher melting point, better mechanical strength, lower environmental impact and lower cost than the others. Therefore, various Fe-based oxygen carriers were developed and extensively employed for chemical looping process in previous studies (Mattisson *et al.*, 2001; Johansson *et al.*,

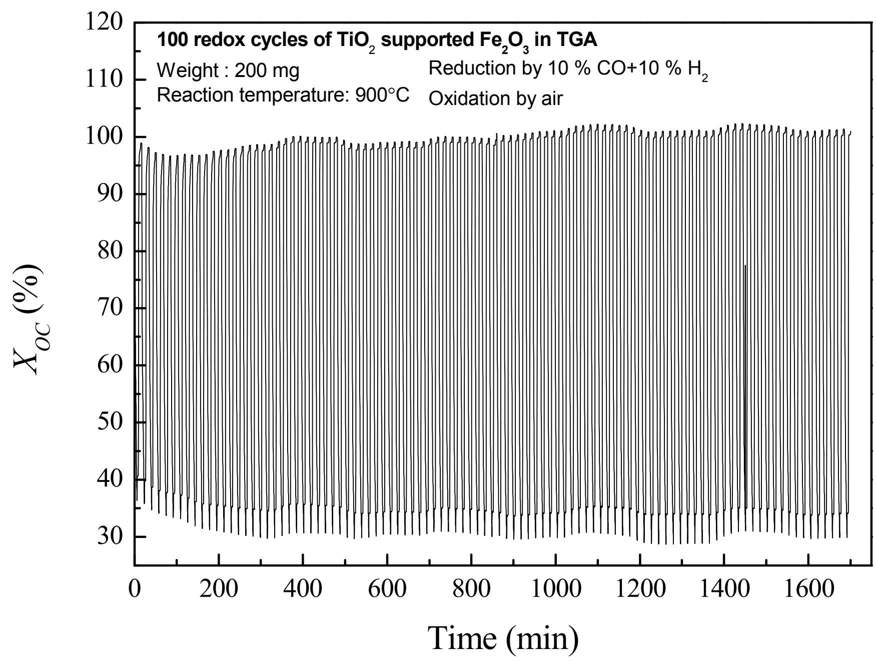

Fig. 2. Degree of conversion of TiO_2 supported Fe_2O_3 oxygen carrier for 100 redox cycles conducted with 10% CO and 10% H_2 for reduction and air for oxidation processes at 900°C.

Table 1. Indexes for evaluation of oxygen carriers.

	Fe_2O_3	NiO	CuO	Mn_3O_4	CoO
Oxygen Capacity (wt %)	30	21	20	20	21
Cost	Low	High	Medium	Medium	Medium
Reactivity	Medium	High	High	Medium	Low
Conversion efficiency of Syngas	Fe_2O_3/Fe_3O_4 100%	Ni/NiO 99.3%	CuO/Cu_2O 100%	Mn_3O_4/MnO 100%	Co/CoO 96.3%
Melting Point (°C)	1275	1452	1026	1260	1480
Mechanical Strength	High	Low	Low	Medium	Medium
Impacts on Environment and Health	Medium	High	Medium	High	High
Support Materials	Al_2O_3 Bentonite MgO $MgAl_2O_4$ Sepiolite SiO_2 TiO_2 YSZ ZrO_2	Al_2O_3 Bentonite MgO $MgAl_2O_4$ $CaAl_2O_4$ CaO $LaAl_{11}O_{18}$ $NiAl_2O_4$ Sepiolite SiO_2 TiO_2 YSZ ZrO_2	Al_2O_3 Bentonite $CuAl_2O_4$ MgO $MgAl_2O_4$ Sepiolite SiO_2 TiO_2 ZrO_2	Al_2O_3 Bentonite MgO $MgAl_2O_4$ $MnAl_2O_4$ Sepiolite SiO_2 TiO_2 ZrO_2	Al_2O_3 MgO $CoAl_2O_4$ YSZ TiO_2

2004; Berguerand and Lyngfelt, 2009; Li *et al.*, 2009; Azis *et al.*, 2010). Moreover, the reduced Fe-based oxygen carriers (Fe or FeO) were reported to be thermodynamically feasible being oxidized by steam to generate hydrogen (Li and Fan, 2008). However, reactivity of Fe-based oxygen carriers is lower comparing to that of Ni-, Mn- and Cu-based oxygen carriers, causing lower combustion efficiency with solid fuels (Mattisson *et al.*, 2004; Adánez *et al.*, 2010; Cuadrat *et al.*, 2011). Ni- and Mn-based oxygen carriers demonstrate high oxygen capacity and reactivity; therefore, are suitable for applications in fluidized bed reactors for chemical looping combustion. However, cost, toxicity and carbon deposition are major drawbacks have to be resolved for Ni- and Mn-based oxygen carriers (Mattisson *et al.*, 2003; Zafar *et al.*, 2005; Johansson *et al.*, 2006). Co-based oxygen carriers provide with high melting point to reduce sintering during chemical looping operation; however, the application of Co-based oxygen carrier is limited to their lower fuel conversion efficiency and inherent high toxicity (Zafar *et al.*, 2006). Cu-based oxygen carriers present similar oxygen capacity and reactivity to Ni- and Mn-based oxygen carriers at lower cost. However, low melting points of Cu-based oxygen carriers limit their long-term operation at high temperatures. Besides, the reduction of Cu-based oxygen carriers is exothermic while other oxygen carriers are reduced endothermically. Therefore, the design of fuel reactor system with regard to Cu-based oxygen carriers should pay special attention on heat transfer concerns (Cao and Pan, 2006).

REACTOR SYSTEMS OF CHEMICAL LOOPING PROCESS

Depending on the mode of oxygen carrier transportation in the fuel reactor, fluidized bed and moving bed reactor systems are developed for the application of chemical looping process. A fluidized bed chemical looping system usually composes of a fuel reactor, an air reactor, an air compressor, loop seals, cyclones and a cold trap as shown in Fig. 3. The oxygen carrier particles are mixed with fuel by fluidizing gas for gas/solid fuel combustion in the fuel reactor. The effluent stream from the fuel reactor consists of mainly CO_2 and H_2O, and high purity CO_2 is yielded after separation of H_2O by the cold trap. The reduced oxygen carrier particles are flown to the inert gas-pressurized loop seal, which avoid gaseous fuel flow into the air reactor, and are transported to the air reactor. The reduced oxygen carrier particles are oxidized by pressurized air in the air reactor for heat generation, and are rose to the cyclone. Small particles are separated from the air reactor by the cyclone, and then the remaining oxygen carrier particles flow back to the fuel reactor through a loop seal for next operation cycle.

The fluidized bed chemical looping systems in different designs, such as circulating fluidized bed, dual circulating fluidized bed and spouted fluidized bed, were operated and studied extensively (Kronberger *et al.*, 2004; de Diego *et al.*, 2007; Berguerand and Lyngfelt, 2008; Gao *et al.*, 2008; Ryu *et al.*, 2008; Lyngfelt, 2011). The fluidized bed systems have been validated to carry out chemical looping combustion at 120 kW level of heat capacity with gaseous fuels and Ni-based oxygen carriers (Bolhàr-Nordenkampf *et al.*, 2009). The particle circulation rates of oxygen carriers for a 1,000 MW chemical looping combustion using methane were estimated to be from 3,000 to 10,000 kg/s, indicating that the circulation of oxygen carrier particles would be a major energy penalty to decrease overall energy efficiency (Fan, 2010). For coal combustion, the consumption of oxygen carriers would be significant

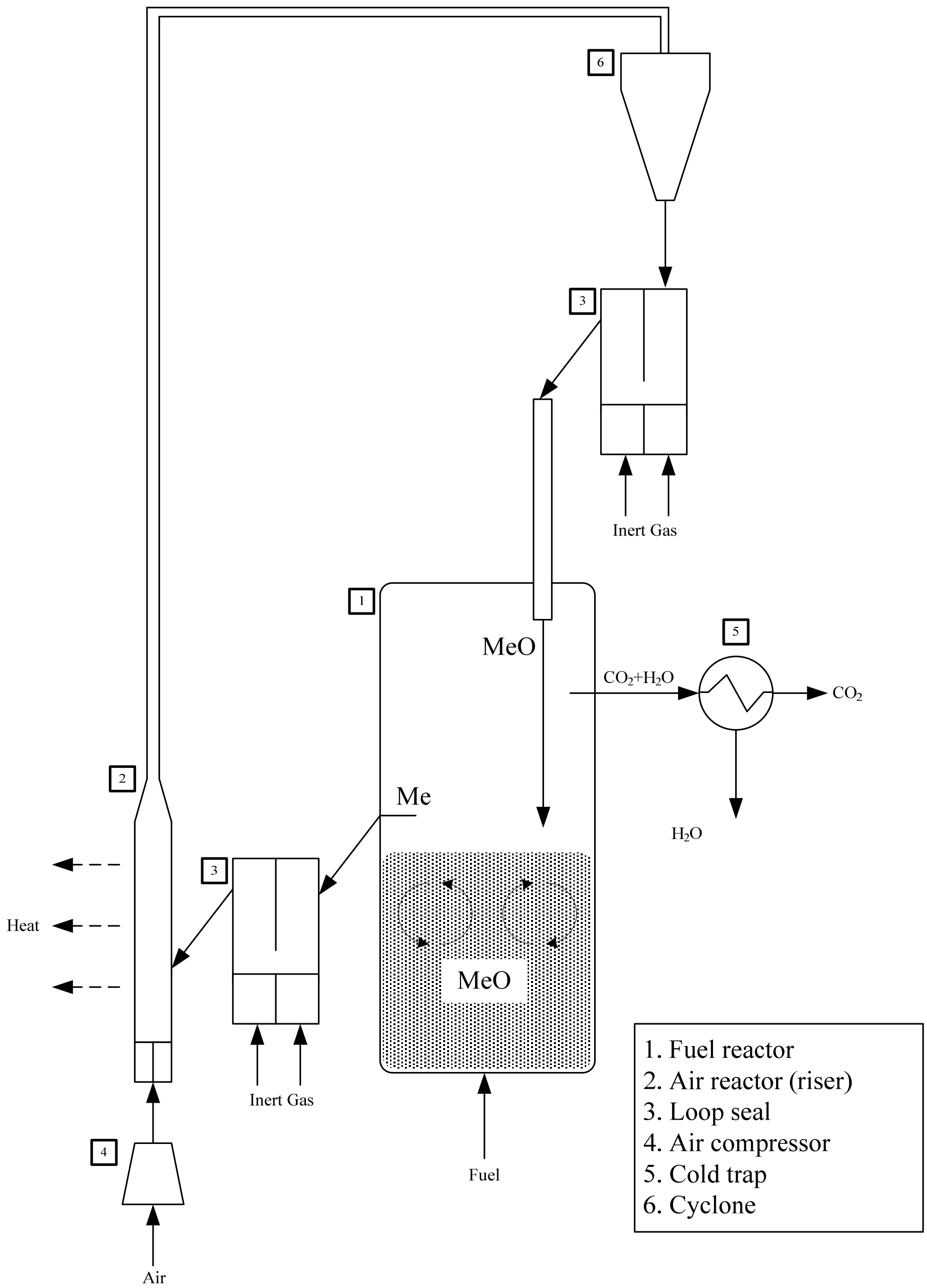

Fig. 3. Scheme of fluidized bed reactor.

because the separation of ash and oxygen carrier particles is difficult; hence, the design of cyclone as carbon stripper is significant for particle separation (Berguerand and Lyngfelt, 2008). Therefore, several low cost oxygen carriers, such as ilmenite, were employed recently for the application of chemical looping process using fluidized bed systems because high consumption of oxygen carrier resulted in high operation cost on oxygen carrier (Leion *et al*., 2008; Proll *et al*., 2009a; Adanez *et al*., 2010)

The schematic diagram for moving bed chemical looping system is shown in Fig. 4 that are composed of a fuel reactor, a hydrogen generator, an air reactor (riser) and loop seals/valves, an air compressor and a cold trap (Sridhar *et al*., 2012). The moving bed chemical looping system was designed for application of Fe-based oxygen carriers moved counter-currently with fuels according to the thermodynamic analysis (Gupta *et al.*, 2007; Li *et al.*, 2010a). The crystalline phase distribution of Fe-based oxygen carriers are Fe_2O_3, Fe_3O_4, FeO and Fe from the top to the bottom in the counter-flow moving bed fuel reactor. The gaseous fuel passed through the fuel reactor from the bottom to the top; therefore, high p_{CO2}/p_{CO} and p_{H2O}/p_{H2} ratios are achieved in the effluent stream (Sridhar *et al.*, 2012). Moreover, higher oxygen capacity in oxygen carriers can be utilized in the moving bed system than that in the fluidized bed system (Li and Fan, 2008). The reduced oxygen carriers are moved by loop seal or mechanical valves purged by inert gas between the fuel reactor and the hydrogen generator.

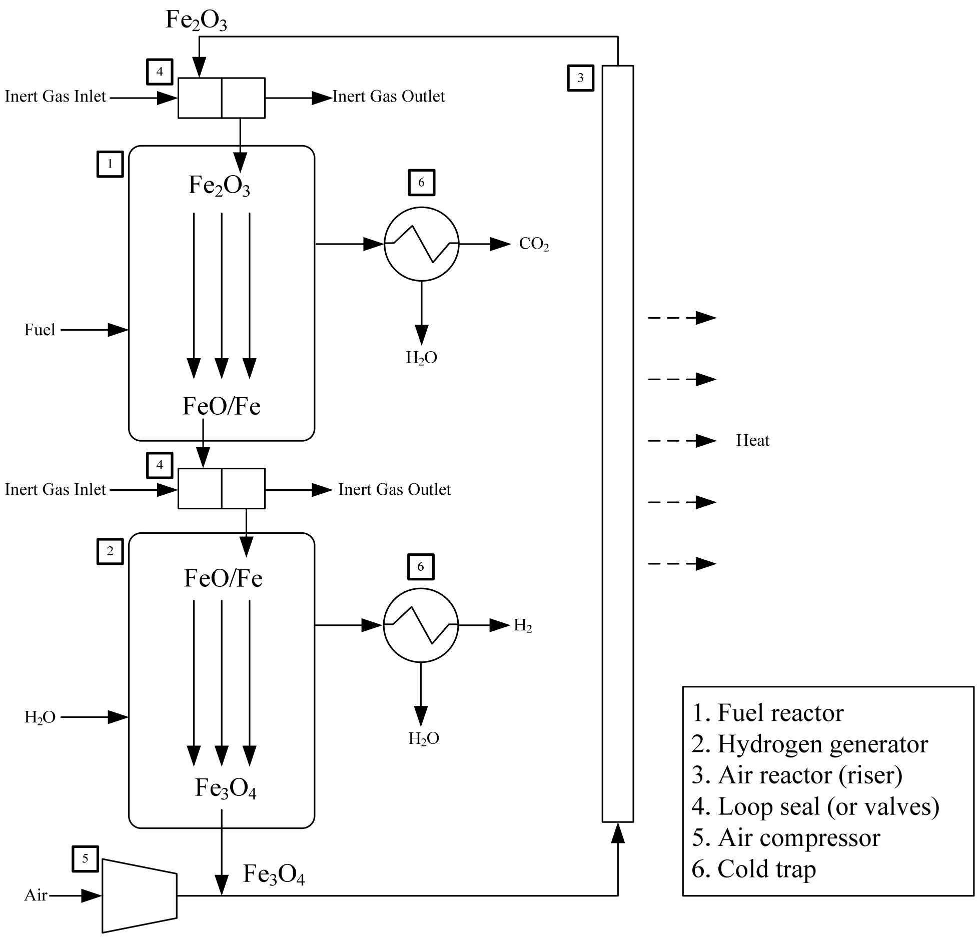

Fig. 4. Scheme of moving bed reactor.

Mechanical valves are high cost and less reliable for a MW level moving bed reactor; therefore, application of gas valves, such as L-valve, J-valve and H-valve, is considered suitable for large scale operation (Fan, 2010). The reduced Fe-based oxygen carriers, FeO/Fe, are moved to hydrogen generator oxidizing by H_2O to generate H_2, and the H_2 in effluent stream can provide to external energy unit or H_2 demanded process after steam separation (Fan *et al.*, 2009). However, the Fe_3O_4 is the final crystalline phase that can not be oxidized by H_2O in the hydrogen generator; hence, the Fe_3O_4 oxygen carrier particles are moved and oxidized by pressurized air in the air reactor accompanied with heat generation. The Fe_2O_3 oxygen carrier particles flow back to the fuel reactor through a loop seal or mechanical valves for next operation cycle.

FUELS FOR CHEMICAL LOOPING PROCESS

For chemical looping process, combustion of gaseous and solid fuels with oxygen carriers exhibited different mechanisms in the fuel reactor. Fuel combustion in chemical looping process is to fully oxidize the fuels to be CO_2 and H_2O by oxygen carriers. The mechanism of gaseous fuel combustion is illustrated in Fig. 5, the gaseous fuel reacted with the oxygen carrier, and the effluent components are expected to be mainly CO_2 and H_2O with fully combustion of fuel. For solid fuel combustion in the fuel reactor, a two-step mechanism is proposed, including gasification and combustion, as illustrated in Fig. 5. Gasification of solid fuel is a partial oxidation process that fixed carbon in the solid fuel is partially oxidized by gasification reactants, such as O_2, H_2O and CO_2 to form CO and/or H_2 as gaseous fuels. The fixed carbon of solid fuels is gasified to CO and H_2 (as H_2O employed to be the gasification reactant) by gasification reactants in the fuel reactor. The CO and H_2 from gasification process is immediately combusted by oxygen carriers in the same manner of gaseous combustion to yield H_2O and CO_2.

Oxygen carrier is reduced in the fuel reactor to provide oxygen for gaseous fuel combustion. Natural gas is one of the primary fuels composed with approximately 90% of methane; hence, methane combustion by chemical looping process is commonly studied for bench scale reactors by previous researchers (Ishida and Jin, 1994; Mattisson *et al.*, 2001; Ryu *et al.*, 2003), and described by reaction (4) with H_2O and CO_2 to be the effluent components.

$$4Me_xO_y + CH_4 \rightarrow 4Me_xO_{y-1} + CO_2 + 2H_2O \quad (4)$$

The thermodynamic analysis for CH_4 as fuel to react with NiO illustrated that CH_4 conversion was between 97.7 and 99.8% for experiments carried out between 700 and 1200°C (Mattisson *et al.*, 2006). However, carbon deposition

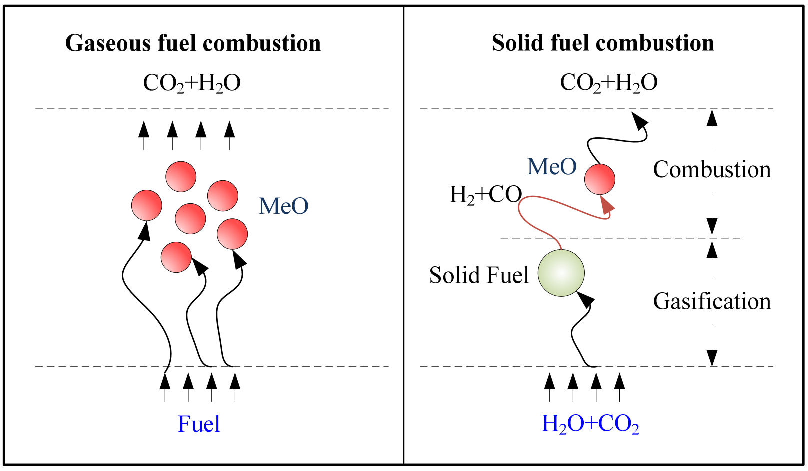

Fig. 5. Mechanisms of gaseous and solid fuels combustion in the fuel reactor.

and incomplete combustion were practically taken place in the fuel reactor (Jin and Ishida, 2002). Two possible pathways have been proposed for carbon deposition, methane decomposition and Boundouard reaction, listed as reactions (5) and (6), respectively (Cho *et al.*, 2005).

Methane decomposition reaction: $CH_4 \rightarrow C + 2H_2$ (5)

Boundouard reaction: $2CO \leftrightarrow C + CO_2$ (6)

Methane decomposition was considered to be the dominant pathway of carbon deposition for chemical looping combustion carried out at higher than 600°C (Claridge *et al.*, 1993). In order to achieve high CO_2 yield as well as high methane combustion efficiency, addition of steam gas can trigger a series of chain reactions, including methane-reforming, carbon gasification, and water gas shift reactions as described by reactions (7), (8) and (9) respectively. Methane would be reformed to be CO and H_2 before it is combusted with oxygen carriers, avoiding carbon deposition by methane decomposition described by reaction (5).

Methane reforming reaction: $CH_4 + H_2O \leftrightarrow CO + 3H_2$ (7)

Carbon gasification reaction: $C + H_2O \rightarrow CO + H_2$ (8)

Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ (9)

As steam introducing at the ratio of $H_2O/CH_4 = 2.0$, no carbon deposition was found on the Ni-based oxygen carriers (Jin and Ishida, 2002). For chemical looping combustion conducted in fluidized bed reactors, insufficient available oxygen in oxygen carrier might also result in carbon deposition (Ryu *et al.*, 2003). For experiments conducted with Ni-based oxygen carriers in the temperature range of 750 and 950°C, carbon was found to be deposited rapidly on oxygen carriers (Cho *et al.*, 2005). For natural gas combustion with Fe-based oxygen carriers in a fluidized bed reactor operated at 950°C, the loading of oxygen carriers was estimated to be 1200 kg/MW in order to achieve fully conversion (Abad *et al.*, 2007a). For methane combustion, the oxygen carrier-to-fuel ratio, ϕ, is proposed as a significant parameter for evaluating available oxygen provided by oxygen carriers on combustion efficiency of methane described in Eq. (10):

$$\phi = \frac{F_{OC}}{4F_{CH4,in}} \quad (10)$$

where F_{OC} is the molar flow rate of oxygen carrier; $F_{CH4,in}$ is molar flow rate of inlet methane. For Ni-based oxygen carrier with regard to methane combustion in a 500 W fluidized bed reactor operated between 800° and 880°C, ϕ has to be higher than 3 for 99% of CH_4 conversion (Adanez *et al.*, 2009). For Cu-based oxygen carriers tested in a 10 kW fluidized bed reactor, full conversion of CH_4 to CO_2 and H_2O was achieved at 800°C as ϕ above 1.5 (de Diego *et al.*, 2007). CO_2 yield was steadily maintained 98% for a 50 kW_{th} fluidized bed reactor system for natural gas combustion with Ni-based oxygen carriers (Ryu *et al.*, 2004). A 140 kW_{th} pilot plant was designed for combustion of natural gas with Ni-based oxygen carriers operated at 950°C, fuel conversion and CO_2 yield were 99 and 94%, respectively (Kolbitsch *et al.*, 2009a). From the literatures with regard to natural gas combustion by chemical looping process, over 90% of CO_2 yield can be easily achieved.

Coal and petroleum coke are composed of high contents of carbon element by ultimate analysis and heat values are estimated to be from 25.1 to 30.9 MJ/kg (25.1 MJ/kg for Indonesian coal; 27.9 MJ/kg for Colombian coal; 30.9 MJ/kg for Mexican petroleum coke) (Leion *et al.*, 2009). Hence, combustion of coal and petroleum coke is the typical power generation means to offer over 40% of electricity demands in the world (IEA, 2010). However, coal and petroleum coke combustions are also a major CO_2 emission source (IPCC, 2007). For improving energy efficiency and reducing CO_2 emissions, integrated gasification combined cycle (IGCC) for coal gasification and combustion is proposed as a promising alternative for electricity generation (Tsatsaronis *et al.*, 1994). Syngas (CO/H_2) is generated through the coal gasification process by the oxidation of coal with O_2 or H_2O. The mechanism of coal gasification to form syngas is usually through Boundouard reaction and carbon gasification reactions described by reactions (6) and (8), respectively. The gasified syngas from coal is combusted by oxygen carriers in the fuel reactor, the syngas combustion is described as reaction (11), H_2O and CO_2 are the expected effluent components.

$$Me_xO_y + CO/H_2 \rightarrow Me_xO_{y-1} + CO_2/H_2O \quad (11)$$

However, IGCC system as a post-combustion technology requires separating CO_2 with additional recovery system that energy penalty is estimated 17.5% resulted in declining of electricity generation efficiency from 46 to 39.3% HHV (Amelio *et al.*, 2007). Chemical looping is proposed to be combined with IGCC for syngas combustion to reduce energy penalty for CO_2 capture, and the exergetic power efficiency was estimated as high as 48.7% by employment of Fe_2O_3 as oxygen carrier in chemical looping combustion (Anheden and Svedberg, 1998). The simulation for coal direct chemical looping combustion was estimated around 50% for electricity generation with over 90% CO_2 capture (Li and Fan, 2008).

Reaction kinetics of oxygen carriers for syngas combustion was analyzed by TGA indicating that reactivity of Cu-based oxygen carriers was higher than Fe- and Ni-based oxygen carriers (Abad *et al.*, 2007b). Based on the results analyzed by TGA, the inventory of oxygen carriers which represented the amount of oxygen carriers for chemical looping operation was estimated to be 19 to 34 kg/MW varied by types of oxygen carriers for power generation with syngas (45% CO and 30% H_2) combustion in fluidized bed systems. Composited oxygen carriers, $NiO/MgAl_2O_4$ and Fe_2O_3/Al_2O_3, have been applied to syngas (50% CO and 50% H_2) combustion in a 300 W fluidized bed reactor with over 99% of conversion that closed to theoretical thermodynamic equilibrium upon the Ni- and Fe-based oxygen carriers (Johansson *et al.*, 2006; Abad *et al.*, 2007b). Moreover, NiO/Al_2O_3 composited oxygen carrier was tested to carry out syngas combustion in a fluidized bed reactor for 50 hours, and maintained 99% of combustion efficiency (Dueso *et al.*, 2009). For syngas combustion, the oxygen carrier-to-fuel ratio, ϕ, is proposed as a significant parameter for evaluating available oxygen provided by oxygen carriers on combustion efficiency of syngas described in Eq. (12):

$$\phi = \frac{F_{OC}}{(x_{H_2} + x_{CO})F_{syngas,in}} \quad (12)$$

where F_{OC} is molar flow rate of oxygen carrier; $F_{syngas,in}$ is molar flow rate of inlet syngas; x_{H2} and x_{CO} are molar fraction of inlet H_2 and CO, respectively. For CuO/Al_2O_3 oxygen carrier fabricated by impregnated method, over 1.5 of oxygen carrier-to-fuel ratio should be maintained for complete syngas combustion in a 500 W fluidized bed reactor (Forero *et al.*, 2009). Therefore, oxygen carrier-to-fuel ratio is a significant parameter for process operation that determines syngas combustion efficiency. Syngas combustion in a moving bed reactor system was investigated by Fe-based oxygen carrier with 99.5% of syngas (44% CO and 29% H_2) conversion was achieved, which is closed to the values simulated by ASPEN PLUS (Li *et al.*, 2009). Degree of conversion with regards to Fe-based oxygen carriers by moving bed operation was approximately 50% that much greater than by fluidized bed operation with around 10% under the same condition (Li *et al.*, 2010a). Thus, moving bed reactors with Fe-based oxygen carrier could be designed for smaller size, comparing to the fluidized bed reactors with similar heat capacity (Li *et al.*, 2009).

Directly combustion of coal by chemical looping process in the fuel reactor is developed for more efficient power generation (Li and Fan, 2008). Steam in the inlet fluidizing stream can sufficiently gasify solid fuels for direct combustion to achieve over 95% of fuel conversion (Gao *et al.*, 2008; Leion *et al.*, 2007). Inlet fluidizing gas containing 100% steam was employed in a fluidized bed reactor system for coal combustion by $NiO/NiAl_2O_4$ oxygen carrier, and 95% of CO_2 yield was achieved for operating temperatures above 900°C (Gao *et al.*, 2008; Shen *et al.*, 2009a). Since Ni-based oxygen carriers demonstrate great performance in reactivity, sulfur contained in solid fuels may react with nickel to form Ni_3S_2 causing deactivation and bed agglomeration (Leion *et al.*, 2009). Fe-based oxygen carriers, such as $Fe_2O_3/MgAl_2O_4$ and natural mineral ilmenite, were used for coal and petroleum coke combustions in fluidized bed reactors to achieved 95% fuel conversion at 950°C, and the solid inventory was estimated to be less than 2,000 kg/MW for residence time less than 5 minutes (Leion *et al.*, 2007). For high combustion efficiency by Fe-based oxygen carriers, the appropriate operating temperature in fuel reactor was suggested higher than 950°C, because both solid fuel gasification and oxygen carrier reduction are endothermic reactions (Leion *et al.*, 2008, 2009). For fluidized bed reactors, the solid inventories of oxygen carriers for solid combustion would much higher than those for gaseous fuel combustion, because part of gasification of solid fuels taken place near the gaseous outlet of the reactor may not be completed (Berguerand and Lyngfelt, 2008, 2009). To achieve fully fuel conversions, high solid inventory was estimated to employ in existed fluidized bed reactors (Leion *et al.*, 2007, 2008). In addition, retrofit the design of fuel reactor to extend the residence time of solid fuel in the fuel reactor is an alternative way to improve the limitation of low gasification rate for direct coal combustion by chemical looping process. The counter-flow current pattern of solid fuel and oxygen carriers was proposed as one of the engineering designs for better CO_2 yield and fuel conversion using Fe-based oxygen carriers (Li and Fan, 2010). For coal and petroleum combustion by chemical looping process, operating temperature, steam fraction of inlet stream and particle separation are significant design and operational factors. Deactivation of oxygen carrier is also needed to be concerned, especially for solid fuels with reactive species like sulfur.

Biomass combustion by chemical looping process is aimed to eliminate biomass wastes and to generate heat simultaneously. The content of biomass such as wood, rice husk, and bagasse are mainly volatile compounds, such as CO, CO_2, CH_4, H_2 and C_nH_m whereas coal and petroleum coke are majorly fixed carbon (Shen *et al*., 2009a, b). The literatures reported by Shen *et al.* indicated that the volatile compounds are decomposed at high temperatures in the fuel reactor, and the biomass combustion by chemical looping process is supposed to achieve higher CO_2 yield with less solid inventory than coal combustion. The combustion of hybrid poplar with Fe-based oxygen carriers in a moving bed reactor was simulated by ASPEN PLUS, the operating temperature in the fuel reactor should be above 900°C to achieve fully biomass conversion and nearly 100% of CO_2 yield (Li *et al*., 2010b). Pine sawdust contained 14.8% of fixed carbon and 75.8% of volatile compounds was combusted by chemical looping process with Fe-based oxygen carriers in a 10 kW_{th} fluidized bed reactors, and achieved 95% of CO_2 yield at 920°C (Shen *et al*., 2009a).

The comprehensive summary for chemical looping process in practical operation is listed in Table 2. The major groups experienced on running chemical looping reactors are selected in this table. The processing capacity of reactors are ranged from 0.01 to 3 MW_{th} indicated that chemical looping technology for energy generation and CO_2 capture is under the level of sub-pilot scale. Gas fuels combustion are generally higher than 95% in CO_2 yield in the effluent stream, thus CO_2 can be sequestrated or utilized without separation process. However, CO_2 yields by solid fuels combustion are not as high as gas fuels combustion, especially using low cost Fe-based oxygen carriers. Hence, solid fuels combustion is aimed to improve fuel combustion efficiency and CO_2 yield in the subsequent works.

FUTURE DEVELOPMENT

Chemical looping process combines with material science, mechanical engineering and chemical engineering, and still under development to be a new energy and environmental technology. The widely developed oxygen carriers are including Ni-, Cu- and Fe-based metal oxides and their composited particles. The development of Ni- and Cu-based oxygen carriers is limited in high cost for plenty of fabrication in spite of their great reactivity for chemical looping process. Fe-based oxygen carriers are the candidates for commercialization of chemical looping process due to economic feasibility. The use of natural mineral like ilmenite as oxygen carrier is a developing research direction for reducing cost on production of oxygen carriers.

Table 2. Summary of chemical looping reactor systems.

Groups	Reactor[1]	Fuel	Oxygen carrier	CO_2 Capture Efficiency	Operation time[2]	References
ALSTOM (USA)	3 MW_{th} CFB-CFB	coal	$CaSO_4$	n.a.	n.a.	Andrus *et al*., 2010
Chalmers University of Technology (Sweden)	10 kW_{th} CFB-BFB	CH_4/natural gas	NiO	94.5–99%	> 1000 hr	Linderholm *et al*., 2008 Linderholm *et al*., 2009 Berguerand and Lyngfelt, 2008 Berguerand and Lyngfelt, 2009 Lyngfelt, 2011
		coal, petroleum coke	ilmenite	68–96%		
Darmstadt University of Technology (Germany)	1 MW_{th} CFB-CFB	coal	ilmenite	n.a.	n.a.	Beal *et al*., 2010
Institute of Carboquimica (CSIC, Spain)	10 kW_{th} CFB-BFB	CH_4	CuO	~100%	200 hr	Adanez *et al*., 2006 De Diego *et al*., 2007
Korean Institute of Energy Research (KIER, Korea)	50 kW_{th} CFB-BFB	CH_4, syngas	NiO, CoO	> 98%	300 hr	Ryu *et al*., 2010
South East U. (China)	10 kW_{th} CFB	coal biomass	NiO Fe_2O_3	95% 76–87%	230 hr	Shen *et al*., 2009a Shen *et al*., 2009b
The Ohio State U. (USA)	2.5 kW_{th} Moving Bed 25 kW_{th} Moving Bed	coal	Fe_2O_3	> 97% n.a.	n.a.	Fan, 2010
	25 kW_{th} Moving Bed	syngas	Fe_2O_3	99.8%	n.a.	Sridhar *et al*., 2012
Technical University of Vienna (Austria)	120 kW_{th} CFB-CFB	syngas	NiO	~95%	390	Kolbitsch *et al*., 2009a Kolbitsch *et al*., 2009b Proll *et al*., 2009a Proll *et al*., 2009b
			ilmenite	~65%		

[1] CFB: circulating fluidized bed; BFB: bubbling fluidized bed.
[2] The operation time is referred by the literature published by Lyngfelt (2011).

However, the reactivity has to be improved to enhance fuel combustion efficiency. The fabrication of oxygen carrier is one of the major costs on preparation of oxygen carriers; therefore, modification of an oxygen carrier through complex procedure is not to recommend for increasing the reactivity of oxygen carrier. To retrofit the design and operation of chemical looping reactors should be considered for application of Fe-based oxygen carriers. The fuel reactor design for longer residence time should be considered due to low reactivity of Fe-based oxygen carriers. Besides, longer residence time also improves the limitation of low gasification rate for direct coal combustion by chemical looping process. The moving bed reactor system with counter-flow pattern between solid fuel and oxygen carrier in the fuel reactor is proposed as one of the alternative designs to increase the residence time. The particle size of oxygen carriers for moving bed operation is from 1.5 to 5.0 mm which is much larger than the particle size of 0.2 mm for fluidized bed reactors system. The movement of oxygen carriers is a significant engineering issue for moving bed system; therefore, the design of sealed valves, such as mechanical valves and loop seals is essential to fluently move oxygen carriers as well as to avoid malfunction on the chemical looping system. The combustion of gas fuels achieved both high fuel conversion and high CO_2 yield by many combinations of oxygen carriers and reactor systems. However, as for solid fuels combustion, the gasification of solid fuel in the fuel reactor is the rate limiting step comparing with combustion of the gasified fuels and oxygen carriers. The addition of gasification reactants, such as CO_2, H_2O and O_2 can enhance the gasification rate of the fixed carbons in these solid fuels. In addition, reactor design for longer residence time is an alternative way to increase the solid fuel conversion efficiency, which mentioned previously. Beside of addition of gasification reactant and retrofit reactor design, chemical looping with oxygen uncoupling (CLOU) is proposed for resolving the problem of gasification rate that oxygen carrier release oxygen gas at specific temperature under oxygen-free atmosphere, thus oxygen gas combusted with solid fuel to avoid gasification step. The problem of low gasification rate is possibly resolved by different mechanism of oxygen releasing by CLOU.

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