Evaluation of Multi-functional Iron-based Carrier from Bauxite Residual for H₂-Rich Syngas Production via Chemical-Looping Gasification

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Abstract: Solid-fueled chemical-looping gasification (SF-CLG) is a chemical looping technology integrated with gasification for poly-generation, i.e. syngas and power production. This flexible platform could avoid costly air separation unit, providing low cost H₂-rich syngas for the production of fuel chemicals, ammonia, methanol, etc. One key to successful SF-CLG is the development of a multi-functional cyclic solid material that can be treated in large quantities. The solid circulating between the two reactors is the means for oxygen, heat, and catalyst transport. This study demonstrates a cost-effective oxygen carrier (OC) developed from Bauxite residual of alumina industry, containing sufficient active content, multi-supporting materials, and promoter. It is proposed to be a cyclic material to transport oxygen and heat from the air reactor to gasifier to promote gasification, and in its reduced form to catalyze internal syngas reforming. The catalytic functions of this OC for char gasification and syngas reforming were validated. Syngas composition and yield, gasification rate, and OC behavior were investigated at different fuel/OC ratio, and by successive redox cycle in a fluidized bed reactor. The compatibility of new composite materials with the proposed auto-thermal SF-CLG was confirmed based on thermodynamics and the material's physical and chemical properties.

Keywords: H₂ rich syngas production; chemical looping gasification; solid fuel; iron-based oxygen carrier

1. Introduction

Chemical looping combustion (CLC) is a highly-efficient technology for fossil fuel combustion and CO₂ capture by avoiding the energy intensive gas separation step [1], and is considered to be one of the most advanced technologies for carbon sequestration according to the U.S. DOE Innovative CO₂ Control Technology Road Map [2]. The application of chemical looping to fuel conversion or syngas production could reduce the energy penalties for air separation or CO₂ capture. This process, schematically described in Fig. 1, consists of two inter-connected reactors, cyclic materials to transport lattice oxygen and heat, and fuels as feedstock. The major products of this process are CO and H₂, while heat for electricity is a by-product. Compared to CLC, the air to fuel ratio of this process is generally lower in order to avoid complete oxidation of the fuel to CO₂ and H₂O [1]. In addition to the cost savings benefits by avoiding air separation process, it also provides a flexible platform to produce power and intermediate syngas for chemical fuels, ammonia, methanol, etc.

With gaseous fuel feed stock, the integration of chemical looping with syngas production yields several types of technologies, such as steam reforming chemical-looping combustion (SR-CLC), auto-thermal chemical looping reforming (a-CLR), and partial oxidation for syngas production [3-7]. These technologies using Ni-based oxygen carrier (OC), have been investigated and successfully demonstrated in continuous facilities with thermal inputs ranging from 500 W to 140 kW [4, 8-9]. Here the Ni-based OCs functions as lattice oxygen transport materials and catalysts for fuel combustion, decomposition and steam reforming.

The same reaction scheme can be used for solid fuels for syngas production. Interest in this technology, using coal and biomass, is currently increasing due to the abundance of these resources [2-3, 10-11]. The gasification agent, usually H₂O or a mix of CO₂ and H₂O, has been used to fluidize bed materials in the fuel reactor (FR). Thus multiple reactions including OC reduction, solid fuel pyrolysis/gasification, and intermediate syngas combustion/reforming are accomplished in one pot. Few efforts had been made to investigate SF-CLG technologies. The use of CaSO₄ for SF-CLG was explored in a TGA apparatus [12]. The current drawback with this material is the generation of sulfurous species, COS and H₂S at high temperature, due to decomposition of CaSO₄. Recently, biomass-fueled CLG was successfully demonstrated in a 10 kW_{th} chemical looping integrated fluidized bed reactor, where tar content in the syngas could be decreased due to the catalytic effect of an iron-based OC [11].

Fig. 1. Chemical-looping gasification for syngas production

Auto-thermal SF-CLG is capable of producing various types of syngas without using the stand-alone *Water-Gas-Shift* (WGS) reactor by selecting proper OC. There are still abundant fundamental and technical challenges need to be addressed before demonstration and commercialization. One key aspect is the development of a cost-effective OC suitable for SF-CLG conditions. The natural ore and materials from solid waste seem to be of great interest [1]. However, the OC's properties required in a CLC process, such as high reactivity and high oxygen transport capacity, chemical and thermal stability, low-cost and environmental compatibility [1, 6, and 13], are of the same importance for SF-CLG process. In CLC process, the presence of an OC would promote in-situ gasification by quick consumption of the gasification inhibitors, i.e., H₂ and CO, around the particles [14-15]. But in SF-CLG process FR is operated at high concentrations of H₂ and CO. Slow gasification became an issue, which would lead to longer residence time and high solid inventory. High resistance to sintering and agglomeration is also important property for OC because higher fuel/OC ratio is adopted for SF-CLG, at which the risk of agglomeration significantly increases. To avoid stand-alone WGS reactor, these solid materials having high selectivity for H₂ production are preferred. Thus, a multi-purpose oxygen carrier capable of promoting solid fuel conversion, *Water-Gas-Shift* reaction (WGSR), and syngas reforming would be the most promising materials for SF-CLG technology.

Maintaining heat balance between the two reactors to achieve a spontaneous process is another challenge for SF-CLG technology. The overall reaction of SF-CLG described in Eqs. (1), can be considered as an exothermic partial oxidation combined with strong endothermic gasification.

Here x and y are the H/C ratio and O/C ratio in the coal, z is the molar ratio of O₂ in air to coal, and m is the steam/coal molar ratio in operation, respectively. The overall exothermic reaction is a prerequisite for the

spontaneous SF-CLG process if there are no any external heat sources. The heat distributions of SF-CLG are typically endothermic in the FR and highly exothermic in the AR. While the circulating material (OC) transports proper amount of O₂ from AR to FR, it should function as an efficient heat transport medium to prevent a significant temperature drop in FR and to obtain favorable kinetics.

The purpose of this study is to explore iron-based materials that can serve as a multi-function OC suitable for auto-thermal SF-CLG technologies. The OC developed from solid waste (Bauxite residual, or red mud, [16]) was selected as a cost-effective circulating material to transport oxygen and heat for solid fuel gasification, while its reduced form was used as a catalyst for syngas reforming. The functions of OC, fuel/OC ratio on syngas composition, OC stability in multiple cycles, and the catalytic function for gasification and WGSR were investigated. A preliminary process analysis of auto-thermal SF-CLG was also performed based on the chemical and physical properties of the red mud OC.

2. Material and methods

2.1 Materials

The red mud oxygen carriers (RM OC) were prepared from Bauxite residual (a solid waste from the alumina industry) using the lab-scale freeze granulation method. The detail preparation method can be found elsewhere [16]. The composition of the raw Bauxite residual, identified by XRF (X-Ray Fluorescence), includes Fe₂O₃, SiO₂, Al₂O₃, TiO₂, CaO, MgO, and a very small amount of alkaline metal (Na₂O and K₂O). The RM OCs used for experiments range from 125-355 μm, and underwent a thermal pretreatment (calcination) at 1,150 °C for 6 hours at atmospheric conditions to achieve sufficient mechanical strength and proper particle morphology. The chemical composition and physical properties of the calcinated red mud OCs are summarized in Table 1. Additionally, a synthesized OC, prepared using commercially available hematite (Fe₂O₃, 5 μm) and alumina oxides (Al₂O₃, 45 μm) at a Fe₂O₃-Al₂O₃ ratio of 1:1, was used as a reference to evaluate the performance of the RM OCs. The production of Fe₂O₃/Al₂O₃ OC followed the same procedure, except for calcination temperature (1400 °C). The synthetic Fe₂O₃/Al₂O₃ OC used for experimentation possesses a particle size of 125-355 μm and a BET surface area of 0.336 m²/g.

To reduce the complexity of the tests, coal char was used as fuel instead of coal. The coal char was prepared from a Western Kentucky coal (USA) using a fixed bed reactor and the proximate and ultimate analyses are shown in Table 2. It was produced in a N₂ flow stream at 700 °C, and the bulk samples were crushed and sieved to 125-355 μm particles before tests.

Table 1
Chemical Composition and Physical Properties of RM OCs

Composition		(wt.%)
Fe ₂ O ₃		51.56
SiO ₂		9.98
Al ₂ O ₃		18.18
TiO ₂		6.47
CaO		7.77
MgO		0.51
Na ₂ O		1.85
K ₂ O		0.18
Balance		3.5
Effective density	g/cm ³	3.734
Crushing strength	N	1.82
BET surface area	m ² /g	0.244

Table 2
Proximate and Ultimate Analyses of Coal Char

Heating Value (MJ/kg)	Proximate Analysis (wt.%)			
	Ash	Volatiles	Fixed carbon	
	27.90	14.72	4.34	80.94
Ultimate Analysis (wt.%)				
C	H	O	N	S
76.70	1.84	2.55	1.65	2.48

2.2 Experimental

A bench-scale fluidized bed facility was used for SF-CLG experiments, which consisted of a fluidized-bed reactor, gas feeding system, flue gas clean-up system, gas analysis system, and computerized data acquisition software and workstation. The schematic diagram of the facility is shown in Fig. 2. The fluidized-bed reactor, fabricated from a stainless steel pipe (SS 310), 38 mm ID and 650 mm height, was heated by an electric furnace. A micro-porous plate placed at 200 mm from the bottom of the reactor was used as sample holder and gas distributor. The reactor was equipped with thermal couples and a pressure transducer to measure the reaction temperature and the pressure drop across the gas distributor and fluidized bed materials. Equipped with different mass flow controllers (MFC, Aeolos QMS403) and steam generator, the gas feeding system allowed the feed of N₂, air, and steam at desired flow rates. A dual piston pump (P-1100, Chrom Tech. Inc.) was used to feed an accurate volume of deionized water to a steam generator, where the feed water was vaporized, and the mixture of feeding gases were preheated to 600 °C before entering the reactor. The feeding of coal char was accomplished with a tube which was inserted from the top of reactor and the tip was 30 mm height above the distributor. To ensure quick feeding, coal char was introduced into the hot bed materials with the help of gaseous feeding stream. The exit gas passes through a cyclone, high temperature filter, cooler, and moisture trap in sequence to remove the fine particles and water condensate. A multi-gas analyzer (Rosemount, X-stream serial), equipped with various channels of O₂, CH₄, CO, CO₂, and H₂, continuously measured the exit gas composition. All signals were recorded in the computerized data acquisition system.

All SF-CLG experiments were carried out in batch operation at 950 °C and atmospheric pressure. For each test, 100 g OC pre-mixed with 150 g fused Al₂O₃ particles (125-355 μm) was used as bed materials. The static bed height was approximately 100 mm to ensure the intermediate gas products had sufficient time to react with the OC particles. During the experiments, OC was first loaded into the reactor and then heated to 950 °C in air stream. When the bed temperature was stabilized, 50 vol.% steam balanced by N₂ (1.5 g/min deionized water and 2.0 L/min N₂) was continuously introduced from the bottom of the reactor. Five minutes later, the reduction began with coal char feed. The superficial velocity in the reactor was 0.24 m/s, which is 3.9 times of minimum fluidizing velocity (U_{mf}) of RM OC particles, and 12 times of that of char particles. Both OC-catalyst and char particles are operated at slow bubbling fluidization regime in reduction step, ensuring the carryover of char particles from the bed materials is quite low.

Fig. 2. Schematic diagram of fluidized bed reactor for SF-CLG experiments

Four series of tests were performed. The aim of the first series was carried out in the fluidized bed facility to experimentally demonstrate the functions of different OCs in aspect of fuel conversion and syngas reforming, including (1) inert Al_2O_3 particles was used to performance external steam-coal char gasification; (2) synthetic $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and RM OCs were applied for SF-CLG, respectively; 2.4 g coal char were used as fuel; (3) SF-CLC experiment was carried out with all operational conditions being the same as the SF-CLG except for more OC (360 g RM OC) used for the purpose of full fuel conversion. For each test, an oxidation process was carried out to burn out the residual carbon and regenerate the OC, allowing an accurate calculation of oxygen and carbon mass balance.

The purpose of the second series of experiments was to examine the catalytic function of RM OC for promoting gasification and WGS. To evaluate promotion in coal char gasification, steam-char gasification was carried out using reduced RM OCs as bed materials. Here the reduced RM OC was obtained at the end of the reduction period of the SF-CLG experiment with a fuel/OC ratio of 2.4 g/100 g. So, the interference of lattice oxygen on fuel conversion could be avoided. A similar experiment was carried out using the reduced synthesized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OC. The investigations of catalytic function for syngas reforming (via the in-situ WGS) were performed in a fixed-bed reactor at various temperatures (300 °C - 950 °C). The reduced RM OC, acid washed sand (SiO_2 , 200 μm) and pure Fe_3O_4 powder (44 μm) were tested individually to compare their reactivity. The same bulk volume of bed material was applied for each test to maintain an identical residence time at approximately 6 s at 700 °C. The inlet gas was 10 vol% CO and 30 vol% steam balanced by N_2 , and the total flow rate was 200 ml/min (standard conditions) for all tests. Here high steam / CO ratio was applied to avoid the Boudouard reaction and further reduction of the reduced OC. The compositions of exit gases at steady conditions were analyzed by a gas chromatograph (GC) for subsequent evaluation.

The aim of the third series of experiments was to qualify the syngas composition, coal char gasification rate, and oxygen loss rate at different fuel/OC ratio when the RM OC was used for SF-CLG process. Different weights of coal char, 0.8 g, 1.6 g, 2.4 g and 3.2 g, were used, while the weight of OC was kept at 100.0 g for each test.

In the fourth series of experiments, a total of 20 redox cycles of SF-CLG were performed to evaluate the behavior of RM OC per cycle. The reduction step was carried out with 50 vol% steam as the gasification agent

(1.5 g/min deionized water and 2.0 L/min N₂) and 2.4 g coal char as fuel. Each reduction period was continued until coal char conversion was completed. The OC was then fully regenerated using diluted air (10 vol. % O₂) before the beginning of the next cycle. Between the oxidizing and the reducing periods, the reactor was purged with 4.0 L/min N₂ stream flow. Due to the thermal effects of reaction, temperature variation was unavoidable. However, the temperature drop during the reduction step and subsequent increase during regeneration step were not higher than 3 °C and 20 °C, respectively. After 20 redox cycles, the OC was cooled to ambient temperature, and characterized by XRD, SEM and XRF.

2.3 Data evaluation

The instantaneous rate of carbon conversion r_c is used to evaluate the gasification of coal char, which denotes the normalized carbon conversion with respect to the amount of residual carbon at time of t :

$$r_c = \frac{dX_c / dt}{1 - X_c} \quad (2)$$

Where X_c is degree of carbon conversion, calculated by

$$X_c = \frac{m_c(t)}{m_{total}} \quad (3)$$

Here m_{total} is the total mass of carbon introduced to the reactor for each test, $m_c(t)$ is the mass of carbon in fuel char that is converted to the gas phase at time t .

Syngas yield per unit of solid fuels feed into reactor can be calculated from

$$V_{syn} = \frac{\int_0^T q_f (y_{CO2} + y_{CO} + y_{H2} + y_{CH4}) dt}{M_{total}} \quad (4)$$

Where q_f is the volumetric flow rate of syngas at the outlet of the reactor under standard conditions, y_i is the molar fraction of components in syngas stream. T denotes the time for full conversion of coal char and M_{total} the total mass of coal char in one experiment. The volume fraction of each gaseous component, Y_i is given by

$$Y_i = \frac{\int_0^T q_f y_i dt}{\int_0^T q_f (y_{CO2} + y_{CO} + y_{H2} + y_{CH4}) dt} \quad (5)$$

OC reactivity and oxygen transport capacity under the well-defined conditions were evaluated for the SF-CLG process. The oxygen loss rate during the reduction period is used as an indicator to depict the cyclic material behavior and stability with multiple redox cycles:

$$r_{oxygen} = \frac{16q_f(2y_{CO2} + y_{CO} - y_{H2})}{22.4} \quad (6)$$

The total oxygen from OC (100 g) for fuel conversion, N_{oxygen} is determined by the integration of the oxygen loss rate with respect to time over the reduction period.

In order to quantify OC's catalytic function for WGSR, the quotient of reaction, J , is introduced to describe the extent of the WGSR as it approaches equilibrium under the experimental conditions.

$$J = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \quad (7)$$

Where P_i is the partial pressure of syngas components, and i are CO_2 , CO , H_2 , and H_2O , respectively.

3. Results and discussion

3.1 Oxygen carrier characterization

SEM images of the fresh RM OC are presented in Fig. 3 (a) and (b), showing spherical particles and porous surface structures. Fig. 4 shows the XRD patterns for the fresh RM OC, where free Fe_2O_3 was identified as the primary active content and the composite salt of $NaAlSiO_4$ as an inert support. The rest of the major components in the raw red mud were not detected, and maybe exist in the form of amorphous phases. Our previous research [17] validated that the active content (free Fe_2O_3) in RM OC could be completely reduced to metallic iron by dry syngas, and all iron-containing phases involved during reduction and regeneration, i.e. Fe_2O_3 , Fe_3O_4 , FeO and Fe , do not react with the support material to form a new spinel phase. Therefore, the unique structure of the RM OC ensures that reaction with coal char-derived syngas will be the reduction of free Fe_2O_3 to Fe_3O_4 , FeO and further metallic iron in sequence. The synthetic Fe_2O_3/Al_2O_3 OC was observed to contain free phases Fe_2O_3 , Al_2O_3 and spinel phase, $FeAlO_3$.

Fig. 3. SEM images of RM OC (a) Fresh particles ($\times 30$), (b) Fresh surface (c) Used after 20 cycles of SF-CLG (showing slight sintering) (d) Used after 20 cycles of SF-CLG (showing development of porosity)

Fig. 4. XRD patterns of RM and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OCs: [A] RM OC, fresh, [B] RM OC, used after 20 redox cycles (oxidized form), [C] RM OC, reduced form in SF-CLG, [D] $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OC, fresh.

3.2 Role of oxygen carrier

In the first series of experiments, SF-CLG using RM and synthetic $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OCs were compared with steam-coal char gasification and SF-CLC. By comparison, the role of RM OC as a lattice oxygen contributor for fuel conversion and an active-sites provider for catalyzed WGSR were identified.

The steam-char external gasification represents the case where the bed material (inert Al_2O_3 particles) provides neither active lattice oxygen for gasification nor active sites for syngas reforming. The resulting H_2/CO ratio of this test is much lower than that of SF-CLG experiment with RM OC. In SF-CLC experiment, active lattice oxygen from RM OC was used to burn off most of the syngas products immediately after coal char was gasified (the gas profiles of SF-CLC and steam-char external gasification can be found in many literatures [18-19], hence they were not shown). There was only a very small volume of flammable gas (lower than 4% in total, N_2 -free) in the product gas stream due to the imperfect contact between the intermediate syngas product and OC. In SF-CLC experiment, the catalytic function of the RM OC for syngas reforming was not present. This is because it was operated with too low a fuel/OC ratio, and the bed materials just acted as a lattice oxygen donor for fuel combustion. According to Eqs. (1), the value of z is zero for steam-char external gasification. So the use of inert sand as bed materials would not to be developed into an auto-thermal process for syngas production. On the contrary, the SF-CLC process can account for the steam/coal molar ratio m to be zero, making the overall reaction an endothermic reaction (fuel combustion). The SF-CLG process is operated at a fuel/OC ratio between SF-CLC and steam-char external gasification (the fuel/OC ratio is infinite). The concentration profiles of SF-CLG with RM OC, as shown in Fig. 5 (a), are composed of two stages. In the first fuel combustion stage, most of the intermediate syngas from gasification is converted to $\text{CO}_2/\text{H}_2\text{O}$ via rapid OC reduction. The second gasification stage is coupled with catalytic syngas reforming, where the CO -rich syngas product is converted to H_2 -rich syngas via catalysis of the reduced RM OCs. In the second stage, the solid conversion rate is lower compared to the fuel combustion stage. But the H_2/CO ratio increased from 4.0 at the beginning of this stage to 10.0 towards the end of reaction, which led to very high H_2 yield over the reduction period. Compared to SF-CLC, the major product of SF-CLG is syngas (the concentration of H_2 is 45.5% and CO is 11.4% in the final syngas product). The overall reaction rate of SF-CLG is lower than SF-CLC (1800 s vs. 1200 s for full char conversion). This is due to the extensive formation of H_2 during the second gasification stage which significantly inhibits char gasification. From the outlet gas concentration, the

rate of oxygen loss from the RM OC was calculated using Eqs. (6), and the resulting profile is shown in Fig. 5 (a). The majority of oxygen loss occurred during the first fuel combustion stage. During the second gasification stage, the oxygen loss rate is quite low and decreases slowly while approaching 0 at 1200 s -1400 s, a time of about 500 s ahead of full char conversion. Thus the first stage is dominated by fuel char gasification, while the second stage is controlled by the catalytic syngas reforming.

Fig. 5(b) shows the mono-peak of syngas profiles of SF-CLG with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OC where the bed materials behave as a lattice oxygen donor for fuel conversion over the whole reduction period. The $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OC did not present strong catalytic function for syngas reforming. Therefore high H_2 and low CO concentrations in the outlet gas were not present together.

Fig. 5. Gas concentration profiles in SF-CLG experiments: (a) using RM OC, (b) using synthetic $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OC. (Mass of OC: 100.0 g; char: 2.4 g; temperature: 950 °C; fluidizing gas: 50 vol% steam balanced by N_2).

3.3 Catalytic function for char gasification and syngas reforming

The SF-CLG experiments reveal the catalytic function of the reduced RM OC for in-situ WGSR via which intensive formation of H_2 occurs taking the advantages of surplus steam used for solid fuel gasification. The catalytic function for WGSR was further qualified for the reduced RM OC using a fixed bed reactor over a wide range of temperature. The reaction quotients, J for the reduced RM OC, Fe_3O_4 particles, and acid washed sand, are shown in Fig. 6 in discrete points. The equilibrium constant of WGSR is plotted in a continuous plot.

For a given temperature, less divergence between the experimental reaction quotients and the equilibrium constant indicates higher reaction activity of the catalyst. For acid washed sand, the values of J are far below the equilibrium curve even at temperatures as high as 1,223 K. The reaction quotients of the reduced RM OC are at least two orders of magnitude higher than the inert sand at all temperatures tested, and reaches the equilibrium values when the temperature exceeded 1,073 K. Pure Fe_3O_4 powder possesses a high surface area of $9.63 \text{ m}^2/\text{g}$ and has very high reaction reactivity, with which thorough equilibrium condition is realized at temperatures as low as 773 K. It is noticeable that the surface area of the reduced RM OC is quite low, $0.42 \text{ m}^2/\text{g}$. Furthermore, the concentration of Fe_3O_4 phases on the RM OC particle surface is diluted by abundant supports. Both aspects definitely result in less active sites available for WGSR. However, Because 850°C - $1,000^\circ\text{C}$ is the typical operational temperature for SF-CLG, the reduced RM OC would effectively act as a WGSR catalyst which can reform the mixture of H_2 , CO , CO_2 , and steam to the equilibrium conditions.

Fig. 6. Reaction quotients of WGSR for various solid materials

Fig. 7 compares the instantaneous gasification rates and the final syngas composition of the steam-char external gasification as the reduced RM and $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OCs were used as bed materials. To avoid any mathematical errors introduced at the beginning and the end of reduction reaction [20], only the steady-state reaction condition ($0.1 < X_c < 0.8$) was used to determine gasification rates. As can be seen, the use of reduced RM OC resulted in higher gasification rate, syngas yield (3.66 L/g vs. 3.35 L/g), H_2 concentration, and H_2/CO ratio (5.7 vs. 3.3). According to the mass balance calculation, negligible lattice oxygen was “extracted” from both OCs during char gasification. So the effects of lattice oxygen loss and the variation in OC’s chemical composition are excluded. For the reduced RM OC, the higher gasification rate may be caused by the existence of Na^+ in the OC particles. The SEM-EDS analysis shows that the concentration of sodium in the reduced RM OC particles range from 1.63 wt.% to 3.56 wt.%, depending on the surface areas. It has been observed that OCs containing a small amount of alkaline metals significantly enhanced the gasification rate in solid-fueled CLC [21-23]. It is believed that, even though the mechanism is not well understood, these OCs containing alkaline metals could provide catalytic effect on char gasification. The alkaline metals are generally vaporized at high temperature ($>900^\circ\text{C}$), and their fraction in the RM OC should decrease after a period of operation. However, Na^+ in the RM OC appears to be immobilized in the form of NaAlSiO_4 (see Fig. 4). The total amount of Na^+ did not show any observable decrease after 20 cycles of SF-CLG experiments. If this is the case, the use of the RM OC will most likely overcome the disadvantage of unrecovered catalyst that is encountered in the traditional catalytic coal gasification.

Fig. 7. Comparison of steam-char gasification with reduced OCs as bed materials: (a) Instantaneous gasification rate, (b) Syngas composition (Mass of reduced OCs: 100.0 g; coal char: 2.4 g; Temperature: 950 °C; Gasification agent: 50 vol% steam)

3.4 Syngas production and solid fuel conversion at different fuel /OC ratios

The compositions of the final syngas products at different fuel/OC ratio are shown in Fig. 8. SF-CLG using RM OC produced H_2 -rich syngas with a wide range of H_2/CO ratio from 2.0-4.5 when fuel/OC ratio is higher than that adopted by CLC process (for 100.0 g RM OC, a full combustion could be realized theoretically at a fuel loading lower than 0.8 g). As fuel/OC ratio declined, the amount of active lattice oxygen available for combustion per unit of solid fuel increased, and H_2 fraction in syngas product, Y_{H_2} , dropped from 51.2% for $R=3.2$ to 21% for $R=0.8$. At the same time, CO_2 fraction, Y_{CO_2} increased from 37.3% to 69%. For the steam-char gasification ($R=G$), CO fraction reached as high as 26.5%. However, the CO fraction of SF-CLG was maintained relatively constant at 10-12%. The syngas yield per unit of solid fuel and H_2/CO ratio are also plotted in Fig. 8, where the two parameters are seen to increase with fuel/OC ratio. The pure steam-char gasification has a slightly lower syngas yield (≈ 2.5 NL /g) than SF-CLG process at the fuel/OC ratio of 3.2 g/100 g because more residual char remains unconverted. Steam-char gasification has the same H_2/CO ratio as the SF-CLG process at a fuel/OC ratio of 0.8 g/100 g, and the difference being that the former yields more H_2 and CO. The generation of CH_4 (less than 0.3%) was negligible in each experiment.

Fig. 9 shows the gasification rate with different fuel/OC ratios. For SF-CLG at a fuel/OC ratio of 0.8 g/100 g and the external gasification (Fuel/sand=2.4g/100g), linear increase of r_c with X_c was seen during the steady reaction conditions ($0.1 < X_c < 0.8$). This phenomenon was attributed to the breaking up of the char structure and the increased porosity [21]. Due to gasification inhibition from H_2 and CO, experiments at fuel/OC ratio=0.8g/100 g showed an improvement in gasification rate by 55% compare to the external gasification. The coal char reactivity in SF-CLG at high fuel/OC ratio could be clearly separated into three different stages which were dominated by different regimes. During the early stage, the gasification rates for all SF-CLG experiments maintained the similar trend, showing a rapid increase from zero to a maximum value. During this stage, coal char gasification proceeded at very low concentrations of the gasification inhibitors (H_2 and CO) [15] because most of the intermediate syngas was combusted by OCs. The second stage appeared after the maximum value during which the gasification rate decreased rapidly with X_c . This phenomenon was attributed to the repaid decrease of lattice oxygen supply from OC and the increase in H_2 concentration, the latter in turn inhibited coal

char gasification [15]. The gasification rate in the third stage increased again linearly with X_c . Coal char gasification in this stage occurred simultaneously with extensive formation of H_2 via WGSR, and for this reason, r_c at high fuel/OC ratios was lower than that of external gasification (Fuel/sand=2.4 g/100 g). More than 95% of final coal char conversion was achieved for all SF-CLG experiments.

Fig. 8. Syngas composition and yield at different fuel/OC ratio (Mass of OC: 100 g RM OC for SF-CLG, and 250 g fused Al_2O_3 particles for steam-char gasification; Coal char: 0.8-3.2 g; Temperature: 950 °C; Gasification agent: 50 vol% steam) Note: R=* represents fuel/OC ratio, R=G is steam-char gasification; the number in bracket is the H_2/CO ratio in the final syngas products.

Fig. 9 Instantaneous carbon conversion rates at different fuel/OC ratio (for the same tests in Fig. 8).

3.5 Syngas production over multiple cycles

Significant changes of mechanical and chemical performances in OC materials are not expected over multi-cycle reaction. Fig. 10 shows that the composition of final syngas products and syngas yield are roughly stable across cyclic experiments. The H_2 concentration is 45.5% in the first cycle, experiences a slight increase in the following cycles, and decreases to 44.9% in the 20th cycle. The CO_2 concentration changes from 42.8% to 43.9% after 20 cycles, while the CO concentration is stabilized at approximately 10-11 %. The gasification rates over

the three consecutive stages, as indicated in Fig. 11, show slight increase with cycle number, and the reason for this phenomenon will be explained in the next section.

Fig. 10. Syngas composition over multiple redox cycles (bed materials: 100 g RM OC; Coal char: 2.4 g; Temperature: 950 °C; Gasification agent: 50 vol% steam)

Fig. 11. Instantaneous carbon conversion rates of SF-CLG experiments over multiple cycles (for the same tests in Figure 10).

3.6 Oxygen loss and the state of reduced OC

In FR of SF-CLG process, the intermediate syngas products react with OC becoming oxidized and reformed. The lattice oxygen loss from OC or the state of reduced OC is the major concerns for syngas production. The reduced OC is expected to contain substantial Fe_3O_4 crystalline phases that could provide sufficient active sites for in-situ WGSR. The formation of FeO or metallic iron should be avoided to reduce the risk of agglomeration or sintering.

Fig. 12 (a) shows the oxygen loss rates of RM OCs at different fuel/OC ratio. Each of curves features a mono-peak with the highest intensity shifting towards the slower apparent OC reaction as the fuel/OC ratio decreases. Fig. 5 (a) demonstrates that the majority of oxygen loss occurred during the initial fuel combustion stage, and a negligible amount of oxygen was available for fuel conversion during the second stage (gasification coupling

355 with catalytic syngas reforming). This observation was similar between different fuel/OC ratios (Fuel/OC ratio
356 ≥ 1.6 g/100 g) and only differed in duration of the initial fuel combustion stage.

Fig. 12. Oxygen loss rate of RM OC at: (a) different OC/fuel ratio and (b) over 20 redox cycles (Bed materials: 100 g OC; Temperature: 950 °C; Gasification agent: 50 vol% steam; fuel loading of each cycle: 2.4 g)

Fig. 12 (b) shows the evolution of oxygen loss profiles in cyclic experiments. Slight activation was observed after 10 cycles. The increased pore size and volume in RM OC were likely the reason for OC activation. The BET surface area before and after cyclic experiments were 0.336 m²/g and 0.354 m²/g respectively, suggesting that the change of surface area was negligible. The pore diameter appreciably increased from 5.03 nm to 8.96 nm and the cumulative pore volume from 0.000653 cm³/g to 0.001296 cm³/g. Generally the larger pore and higher pore volume allow the reactant gases to diffuse more rapidly and deeper inside the solid material for a higher reaction rate. The observation in **Fig. 12 (b)** supports this concept. The improved OC texture played a role in the early stage of reaction, i.e. the increase in reactivity with cycle occurs at the beginning of reduction period. While after that, the oxygen loss rate maintained the same for all cycles. **Fig. 3 (c) - (d)** show the SEM images of the used RM OCs. Both increases in porosity and sintering were founded simultaneously in different areas of particle surface. Gradual segregation of iron element during redox cycle, which has been observed in other natural iron-based OCs [21], may cause variation in OCs reactivity. However, the SEM-EDX analyses for the fresh and used samples (full oxidized form) did not show appreciable changes in Fe- and O- shares on the particle surface. In addition, XRD patterns (see **Fig. 4**, spectrum B) suggested that the crystalline phases of the active content (free Fe₂O₃) and the support were not altered by the cyclic redox reaction. Furthermore, the chemical compositions (given in **Table 1**) also remained the same for the fresh and used samples. The previous section showed that coal char gasification rate gradually increased with cycle number in the cyclic experiments (**Fig. 11**). This can be attributed to the OC's activation. However, the disadvantage caused by OC activation was the slight decrease of H₂ yield.

Fig. 13. State of iron-containing phase in the reduced OCs

Fig. 13 plots the degree of RM OCs' conversion for SF-CLG/CLC experiments at different fuel/OC ratio and cycles, and the results from the synthesized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OCs (fuel /OC ratio is 2.4 g/100 g) was given. The weight loss from OCs was normalized with respect to the reduction of Fe_2O_3 to Fe_3O_4 . The ordinate value in plot less than 1.0 means the OC reduction is confined in the range of Fe_2O_3 to Fe_3O_4 , while greater than 1.0 means that the iron-containing phase of OC is reduced beyond Fe_3O_4 . For the synthesized $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ OC, the active content was reduced far beyond Fe_3O_4 (the lattice oxygen consumed corresponds to a weight loss of 6.2% of active content). In the case of SF-CLC with RM OC, the reduction was confined in the range of Fe_3O_4 , leaving some amount of carriers unused. The results of SF-CLG showed that the increase of the fuel /OC ratio (when ≥ 1.6 g /100 g) and the cyclic redox reaction (fuel /OC ratio=2.4 g /100 g) do not evidently impact the availability of lattice oxygen. A slight increase in the calculated N_{oxygen} from 3.8% to 4.1% was seen as the fuel/OC ratio increased from 1.6 g /100 g to 3.2 g /100 g. After 20 redox cycles, the value of N_{oxygen} at fuel/OC ratio of 2.4 g/100 g increased from 4.0% to 4.29%. All these values are comparable to the theoretical weight loss (3.4 wt. %) as Fe_2O_3 is reduced to Fe_3O_4 , indicating that the oxygen loss from the RM OCs were mostly ascribed to the reduction of Fe_2O_3 to Fe_3O_4 . The XRD patterns of the reduced RM OC (in **Fig. 4**, Spectrum C) showed very strong Fe_3O_4 characteristic peaks (the amount of FeO is so small to distinguish in the spectrum). The extensive formation of magnetite in the reduction period of SF-CLG was closely associated with the following two reversible reactions which take place on the RM OC particle surface to avoid deep reduction and severe agglomeration or sintering [17].

3.7 Feasibility of auto-thermal SF-CLG

For the auto-thermal SF-CLG process, the heat transport from AR to FR via OCs is very crucial in practical sense. The OC's melting point and heat capacity are the most important physical properties affecting heat transport between the two reactors. A high melting point is preferred for the circulating materials; otherwise, OC agglomeration or sintering will cause problems in solid circulation and chemical deactivation. The melting point of RM OC (the reduced form) was experimentally determined at 1421 °C, which meets the required temperature stability defined by Kyoun-Soo Kang, et.al. [24]. So, if 70% of the melting temperature is

estimated to be the starting point of thermal sintering, 1000 °C could be considered an allowable temperature of the FR to avoid agglomeration for the RM OC.

On the other hand, for a given fuel/air ratio, the temperature drop in the FR should be low enough to obtain favorable kinetics. A high OC heat capacity is expected, with which enough heat could be transported from the AR to FR to support a strong endothermic gasification. In our analysis, RM OC is considered a mixture of Fe_2O_3 , Fe_3O_4 , Al_2O_3 , SiO_2 , etc, and thus its specific heat capacity (effective specific heat capacities of mixture, C_p) is the mass-weighted average of specific heat capacities of the constituent substances. The predicted values of C_p for reduced and oxidized RM OCs are shown as continuous curves in Figure 14. The predicted values of C_p are validated by TGA-DSC measurements, as shown as discrete points in Figure 14. It can be seen that at high temperature (> 653 K), the measured values are in agreement with the predicted values.

Fig. 14. Specific heat capacity of RM OC

The feasibility of auto-thermal SF-CLG using RM OC was examined based on its physical properties and thermodynamics using Aspen software. The preliminary process simulation specially focused on the functions of RM OC as oxygen and heat carriers, and the combined cycle and heat integration for power generation, and ash separation were not considered in detail. The SF-CLG process for simulation exactly possesses the same flow diagram as shown in Fig. 1, and an ideal cyclone, assumed 100% cut efficiency, was added at the outlet of the AR to separate the regenerated OCs from hot spent air stream.

PRB coal was selected as fuel with a feed rate of 100 kg/h. The air to coal ratio was roughly fixed at low value of 5.5-6.0 kg/kg to ensure partial fuel combustion in the FR and an overall exothermic reaction. In the AR, fresh air was preheated to 370 °C; the firing temperature of the AR was specified at 1,038 °C. In the FR, steam flow rate and temperature were specified at 200 kg/h and 315 °C. In the case calculation, 1,000 °C limits was enforced for reactor temperature to avoid agglomeration issue.

In five cases studies, OC circulation rate is changed to investigate the FR temperature and the syngas composition. Gibbs globe equilibrium module is adopted for FR reaction, and the reduction of active content Fe_2O_3 to Fe_3O_4 in OC is enforced and 100% solid fuel conversion as well. The AR adopts stoic reaction module for 100% OC regeneration. In iteration, heat balances between the two reactors and that for each reactor were realized. Fig. 15 and Table 3 show the resulting solid circulation rate, OC conversion, air supply and syngas composition against FR temperature. RM OC circulation rate had strong effects on FR temperature, i.e, when OC/coal ratio increased from 75 to 235, the temperature difference between the FR and AR shrunked quickly from 150 °C to 38 °C. However, the air flow for full regeneration of RM OC varied only between 566

kg/h to 603 kg/h, due to the slight increase of total lattice oxygen used for fuel conversion as the FR temperature increased. High circulation rate obviously benefits the kinetics of solid fuel conversion, but this requires larger reactor and higher energy consumption for solid transportation. As suggested by Table 3, the production of syngas showed quiet stability in syngas yield and composition when OC circulation changed. The syngas products from the present process achieved a rough H₂: CO molar ratio of 2:1 that could meet the requirement for the downstream liquid fuel production. So the trade-off between kinetics of solid fuel conversion and OC circulation is the key for process control.

Fig. 15. RM OC circulation rate (OC/coal), air supply and OC conversion (X_{OC}) against FR temperature

Table 3
Syngas composition vs. FR temperature

Tem. of FR (°C)	870	900	925	955	982
Syngas, wet (kg/h)	412	414	416	418	420
Composition					
H ₂ O (%)	12.29	12.41	12.54	12.66	12.78
CO (%)	0.79	0.80	0.80	0.80	0.80
H ₂ (%)	2.21	2.09	1.96	1.84	1.72
CO ₂ (%)	3.70	3.69	3.69	3.68	3.69
H ₂ /CO	2.80	2.61	2.44	2.29	2.15

4. Conclusions

A multi-functional circulating material developed from a solid waste of alumina industry (red mud) was demonstrated for SF-CLG process. It contained sufficient active iron oxides and the proper heat capacity to transport oxygen and heat to promote endothermic gasification. Its reduced forms could provide active sites for in-situ syngas reforming. Our conclusions are as follows

- (1) The RM OC plays a unique role in SF-CLG process. The early reduction stage of SF-CLG is dominated by fast fuel combustion and OC reduction, and the later stage by a strong catalytic WGS coupled with gasification.
- (2) It is confirmed that the reduced RM OC possesses a strong catalytic function for WGS which quickly shift the wet intermediate syngas towards thermodynamic equilibrium of the operational temperature. The abundance of magnetite (Fe₃O₄) in the reduced RM OC accounts for this strong catalytic function.

- Compared to the synthesized reference OC, RM OC could promote char gasification despite the absence of lattice oxygen transfer during solid fuel conversion.
- (3) The physical properties and oxygen transportability of RM OC show stability during multiple redox cycles. The degree of reduction of RM OC is not far beyond Fe_3O_4 across a wide range of fuel/OC ratios. Taking advantage of these characteristics, process design and operation for SF-CLG could be possibly simplified.
- (4) With high melting point and proper heat capacity, RM OC can be operated at temperature as high as 1000°C of the fuel reactor, and also can transport enough heat from the air to the fuel reactors to enable endothermic gasification at appreciable kinetics, making the auto-thermal SF-CLG a favorable process.

Acknowledgements

The authors thank US Department of Energy for its financial support on the project which focuses on the demonstration of chemical looping gasification technology. The Kentucky Energy and Environment Cabinet Department for Energy (Development and Independence Grant Program) and Energy Research the Carbon Management Research Group consortium at the University of Kentucky Center for Applied Energy (UKy-CAER) are also greatly appreciated. It is also grateful to Megan Combs (UKy-CAER) for improving the quality of language and figures.

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