On the High-Gasification Rate of Brazilian Manganese Ore in Chemical-Looping Combustion (CLC) for Solid Fuels

Peter Frohn
School of Mechanical Engineering, University of Siegen, D-57068 Siegen, Germany

Mehdi Arjmand, Golnar Azimi, and Henrik Leion
Dept. of Chemical and Biological Engineering, Division of Environmental Inorganic Chemistry, Chalmers
University of Technology, SE-412 96 Göteborg, Sweden

Tobias Mattisson and Anders Lyngfelt
Dept. of Energy and Environment, Division of Energy Technology, Chalmers University of Technology,
SE-412 96 Göteborg, Sweden

DOI 10.1002/aic.14168

The high rate of char gasification observed when using a Brazilian manganese ore as compared to ilmenite is investigated in a batch fluidized-bed reactor. Experiments were carried out at 970°C using petroleum coke, coal and wood char as fuel with a 50% H_2O in N_2 as fluidizing gas. A manufactured manganese oxygen carrier was also used, however, which presented a slower char conversion rate than the manganese ore. It is concluded that decrease in H_2 inhibition and oxygen release are unlikely to be the main responsible mechanisms for the ore's unexpected gasification rate. The ore was also mixed in different ratios with ilmenite and it was observed that the presence of even small amounts of ore in the bed resulted in increased gasification rate. Thus, the high-gasification rate for the manganese ore could be due to a contribution from the impurities in the ore by catalyzing the gasification reaction. © 2013 American Institute of Chemical Engineers *AIChE J*, 59: 4346–4354, 2013

Keywords: CO_2-capture, chemical-looping combustion (CLC), manganese ore, ilmenite, solid fuels

Introduction

As suggested by the intergovernmental panel on climate control (IPCC), a 50–85% reduction in total CO_2 emission by 2050 is necessary to limit the anticipated global temperature rise to 2°C.[1] One option to reduce emissions is to capture CO_2 produced in combustion processes from power plants in order to store it, generally called carbon capture and storage (CCS). However, most capture methods have a significant energy penalty due to the gas separation steps involved. Thus, the overall efficiency of power generation process decreases by approximately 7–15% using conventional capture techniques in comparison to combustion without carbon capture. One solution for this problem is chemical-looping combustion (CLC).[2]

The main principle of chemical-looping combustion is based on two separated reactors, an air and a fuel reactor as shown in Figure 1. An oxygen carrier, which in most cases is a metal oxide, is circulated between the reactors. Compared to normal combustion, the fuel is not burnt in air; instead the oxygen carrier supplies the necessary oxygen for conversion of the fuel. The carrier is then reoxidized in a separate air reactor and is ready for the next cycle. The advantage is given by the prevention of nitrogen mixing with the CO_2 from the fuel. Thus, the flue gases from the fuel reactor consist ideally of only CO_2 and water steam, from which pure CO_2 is obtained after condensation of water.

The chemical reaction in the fuel reactor is either endothermic or exothermic depending on the fuel and the oxygen carrier, while the oxidation in the air reactor is strongly exothermic.[3] The occurring reactions are as follows

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

$$2Me_xO_{y-1}+O_2 \rightarrow 2Me_xO_y \tag{2}$$

By combining the reduction (Eq. 1) with the oxidation (Eq. 2), it is seen that the overall reaction is identical with conventional combustion process, which shows that the CLC process does not entail any direct energy penalty for CO_2 separation.

Chemical-looping combustion (CLC) was first introduced by Lewis and Gilliland[4] to produce a pure stream of CO_2. In 1994, Ishida and Jin[5] suggested the technique for CO_2-capture. In 2001, Lyngfelt et al.,[6] proposed a unit consisting of two interconnected fluidized-bed units to implement chemical-looping combustion. The process was first demonstrated for gaseous fuels in 2003.[7] Later, Kolbitsch et al[8] designed, built and operated a 120 kW unit consisting of two circulating

---

Correspondence concerning this article should be addressed to M. Arjmand at arjmand@chalmers.se.

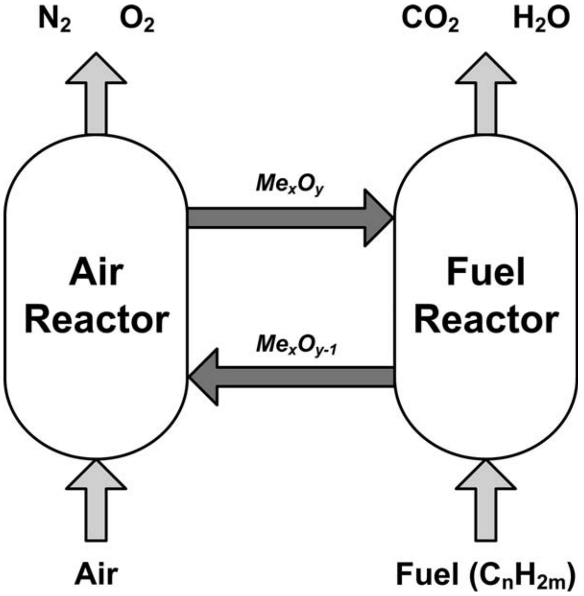

Figure 1. Principle of the chemical-looping combustion (CLC) process.

fluidized-bed reactors. Chemical-looping combustion operations using solid fuels has been investigated by Berguerand and Lyngfelt,[9] Cuadrat et al.,[10] and Markström et al.[11] Overviews of current achievements in CLC are given by Lyngfelt,[12,13] Hossain and de Lasa[14] and Adanez et al.[15]

In general, the use of solid fuels in CLC requires an additional step compared to the combustion of gaseous fuels. Solid fuel conversion through direct solid-solid contact between the oxygen carrier and the fuel is not expected to occur at an appreciable rate. Hence, there are two options for using solid fuels in this case, CLC with gasification of solid fuels[16] and chemical-looping with oxygen uncoupling (CLOU).[17] In the case of CLOU, an oxygen carrier provides gaseous oxygen during the reduction phase according to Eq. 3, and the solid fuel is burned in the uncoupled oxygen

$$Me_xO_y \rightarrow Me_xO_{y-2}+O_2 \tag{3}$$

However, the disadvantages with CLOU are the limited range of appropriate oxygen carriers and the limitation in operational conditions.[17] As CLOU oxygen carriers, CuO[18,19] but also perovskites[20,21] or combined Mn-Fe oxides[22,23] can be mentioned.

An alternative to CLOU is CLC with gasification of solid fuels where the char remaining after devolatilization is gasified by steam, producing CO and H_2, which can then react with the oxygen carrier. For gasification, either CO_2 or steam has to be introduced into the fuel reactor to gasify the solid fuel, according to

$$C+H_2O \leftrightarrow CO+H_2 \tag{4}$$

$$C+CO_2 \leftrightarrow 2CO \tag{5}$$

The oxygen carrier then converts the gaseous products produced according to Eq. 1. The conversion of gaseous products is very rapid whereas the gasification reactions take place at a much lower rate. Furthermore, the carbon gasification rate is inhibited by the H_2 and CO present during the gasification. It is assumed that H_2 forms complexes at free carbon surfaces.[24] This hinders the steam from gasifying the char to gaseous products, e.g., H_2 and CO according to Eq. 4. Thus, it would be advantageous to find ways to suppress the H_2 inhibition effect. This may be achieved with an oxygen carrier which reacts and removes the H_2 from the reaction zone. Similar is the case for CO, although it likely has less influence on steam gasification.[25] Additionally, the water-gas-shift reaction occurs in the gas phase during gasification according to Eq. 6, for which the equilibrium depends on the operational temperature

$$CO+H_2O \leftrightarrow CO_2+H_2 \tag{6}$$

Oxygen carriers for chemical-looping combustion are usually metal oxides provided in the form of particles. In general, important characteristics of the oxygen carriers are fuel conversion, mechanical strength, lifetime, environmental impact, reduction and oxidation rates and cost.[26] One type of oxygen carriers are manufactured particles. They often consist of the active oxides, such as NiO, CuO, Fe_2O_3 or Mn_3O_4, but also of an inert component that improves the physical properties of the compound, such as surface contact and stability. Typical inert materials are magnesium, MgO, SiO_2, TiO_2, ZrO_2, Al_2O_3 or $MgAl_2O_4$. However, for CLC with solid fuels, the lifetime of the oxygen carrier may be affected by the deactivation caused by ash or loss of material with the ash during separation from the oxygen carrier. Thus, less expensive natural minerals with sufficient reactivity are favored compared to more costly manufactured oxygen carriers. For instance, the use of ilmenite (an iron-titanium mineral) has shown comparable rates of steam gasification to a manufactured $MgAl_2O_4$-supported Fe_2O_3 oxygen carrier.[27] Another cheap natural mineral which can be used as oxygen carrier is manganese ore. Leion et al.[28] and Fossdal et al.,[29] investigated the use of several manganese ores and manganese-based industrial byproducts, however, using gaseous fuels. More recently, operation in a 10 kW CLC unit for solid fuel using a Brazilian manganese ore showed an unexpected and significant effect on the rate of steam gasification of char.[30] Later, Arjmand et al.,[31] quantified the increase in rate of steam gasification for the same Brazilian manganese ore and showed that the char conversion rate increased by a factor of five compared to ilmenite. This work attempts to further investigate the high rate of gasification for the Brazilian manganese ore in CLC for solid fuels.

Experimental

Materials used in this work

Table 1 summarizes the physical properties and characteristics of the Brazilian manganese ore and Norwegian ilmenite concentrate used as oxygen carrier in this investigation. Table 2 shows the elemental analysis of the manganese ore and ilmenite concentrate. The ilmenite had been activated using syngas, for 30 cycles at 900°C, and in this way, a stable reactivity had been achieved.[32,33] For reasons of comparison, a manufactured Mn-oxide oxygen carrier consisting of Mn_3O_4 and MgO-stabilized ZrO_2 as support (40/60 wt %) is also used in this work. This oxygen carrier was fabricated by freeze-granulation and was sintered at 1150°C for 6 h. For further details about the freeze-granulation method and properties of the Mn-oxide oxygen carrier, see Zafar et al.[34] All oxygen carrier materials were sieved through stainless steel screens to yield particles in the range of 125–180 μm. The proximate and ultimate analyses of the three different fuels

Table 1. Physical Properties and Characteristics of the Brazilian Manganese Ore and Norwegian Ilmenite Concentrate

	Brazilian manganese ore	Norwegian ilmenite concentrate
Origin (Supplier)	Buritirama (Mineração Buritirama S. A.)	Tellnes (Titania A/S)
Effective density [g/cm^3]	3.15	3.8
BET specific surface area [m^2/g]	3.13	0.11
Crushing strength [N]	1.1	3.7

used in this work are presented in Table 3. The fuel particles were sieved to a size range of 180–250 μm.

Experimental setup and procedure

A laboratory batch reactor system consisting of a fluidized-bed reactor, a heating oven, mass flow regulators for gas distribution and a Rosemount NGA-2000 gas analyzer is used. The analyzer is connected to a computer to record gas concentrations, temperature and flow rate. The system also includes a steam generator for the solid fuel gasification and a cooler to condense the water after the reactor. The general layout of the system is shown in Figure 2. The experiments in this setup can simulate both air and fuel reactors in one reactor, i.e., the batch reactor. Hence, reduction and oxidation periods are alternated using automatic valves. The fluidized-bed reactor had a cylindrical shape holding a porous quartz plate which supports the bed, according to Figure 3. The temperature is measured using two Pentronic CrAl/NiAl enclosed inconel-600 thermocouples below and above the porous plate.

In the general experimental procedure in this work, a bed mass of 20 g of Brazilian manganese ore is used. The Brazilian manganese ore was previously used by Linderholm et al.,[30] in the 10 kW CLC unit for 10 h. The bed temperature was adjusted to 970 ± 5°C referring to the temperature measurement above the porous plate. An inlet flow rate of 900 mL$_N$/min was used during oxidation, reduction and inert periods. The reduction period uses a 50/50% mixture of nitrogen and steam. As fuel, 0.1 g of Mexican petroleum coke is generally used which is introduced from top of the reactor during the reduction period. A nitrogen sweeping gas with a flow rate of 300 mL$_N$/min accompanied the introduction of the fuel at the top of the reactor to ensure that the fuel reaches the reaction zone of the reactor.

The first series of experiments compares the rate of steam gasification of the Brazilian manganese ore to Norwegian ilmenite concentrate which is a well-known oxygen carrier for CLC applications using solid fuels.[35] The rate of steam gasification is also compared with the Mn-oxide oxygen carrier. The rate of char gasification in case of manganese ore and ilmenite oxygen carriers are compared using three different fuels: Mexican petroleum coke, Swedish wood char and Colombian coal (El Cerrejon). The second series of experiments investigates the effect of mass ratio of manganese ore to fuel in the range of 50 and 400 in order to observe a possible contribution of oxygen release from the manganese ore. This was done using two different bed masses, i.e., 20 and 40 g of manganese ore. In the third series of experiments, the manganese ore is gradually introduced to a bed of ilmenite. Thus, different bed mixture ratios from 1 to 60 wt % of manganese ore in ilmenite were investigated.

Table 2. Elemental Analysis of the Brazilian Manganese Ore and Norwegian Ilmenite Concentrate

	Content [wt. %]	
	Brazilian manganese ore	Norwegian ilmenite concentrate
SiO_2	9.17	2.05
Al_2O_3	7.65	0.5
CaO	0.291	0.33
Fe_2O_3	8.02	53.9
K_2O	1.25	<0.06
MgO	0.661	3.9
MnO	68.8	0.15
Na_2O	<0.05	0.06
P_2O_5	0.129	0.05
TiO_2	0.661	44.90

Data evaluation

The fraction of char conversion X_C, during solid fuel experiments is defined as

$$X_C=\frac{m_C(t)}{m_{tot}} \tag{7}$$

where $m_C(t)$ is the mass of carbon converted at time t and m_{tot} is the cumulative amount of carbon converted during one cycle. Both $m_C(t)$ and m_{tot} are determined by the integration of the concentration of carbon containing gases using Eq. 7

$$m_C(t)=\int_{t_0}^{t_1} \dot{n}_{out} M_C (y_{CO_2}+y_{CO}+y_{CH_4})dt \tag{8}$$

where M_C is the molar mass of carbon. To determine m_{tot}, Eq. 7 is integrated to the end of the reduction period. This was done in order to avoid the soot/carbon stuck on the walls of the reactor or in the filter during fuel introduction from influencing the char conversion rate in the bed. This has been confirmed in the current experimental setup from the insignificant carbon burn-off in the subsequent oxidation cycle (<5% of the total converted carbon), shown by the CO and/or CO_2 concentrations in the subsequent oxidation period.[27]

The instantaneous rate of char conversion based on the remaining nonreacted carbon in the bed r_{inst}, is calculated as[25]

$$r_{inst}=\frac{dX_C/dt}{1-X_C} \tag{9}$$

In this work, the gasification rate defined in Eq. 9 is mostly used to express the rate of char conversion. The char conversion rate is also demonstrated by the arithmetic average of the instantaneous rate $\bar{r}_{inst}$, calculated for intervals of 0.02 of carbon conversion X_C, and between X_C of 0.3 and 0.7. The lower limit is chosen since the reaction is mainly

Table 3. Proximate and Ultimate Analysis for Mexican Petroleum Coke, Colombian Coal (El Cerrejon) and Swedish Wood Char, all Values are in Weight Percentage

		Proximate analysis [wt. %] (as received)			Ultimate analysis [wt. %, d.a.f.]				
Fuel	H_i [MJ/kg]	Volatiles	Moisture	Ash	C	H	S	N	O
Swedish wood char	28.7	22.9	4.3	3.2	81.5	3.3	-	0.6	14.6
Colombian coal	21.9	33.0	2.3	8.8	65.8	3.3	0.6	1.6	17.6
Mexican petroleum coke	31.7	10.0	8.0	0.5	81.3	2.9	6	0.9	0.5

influenced by the release of volatiles during the early stages of the reduction phase. The higher limit is chosen to avoid effects such as particles being stuck in the filter having influence on the gasification rate close to the end of the reduction period.[27]

Results

Rate of steam gasification

The flue gas concentration profiles are shown in Figure 4 for a representative cycle with Brazilian manganese ore using Mexican petroleum coke as fuel. The concentration profiles show a peak in the beginning of the cycle due to the release of volatiles. The carbon dioxide concentration has its peak during the first third of the experiment and reaches a value close to 8%. Due to the dilution of fluidization gases with the sweeping gas from top of the reactor during solid fuel experiments, the in-reactor concentrations should be higher.

The instantaneous gasification rate (Eq. 9) is shown in Figure 5 for the same cycle as in Figure 4. The first part of the conversion, between the degrees of carbon conversion of 0 and 0.3, is mainly influenced by experimental startup, meaning injection of fuel and the release of volatiles. This also explains the peak in the beginning which indicates the release of those volatiles, mainly methane. Between fuel conversion degrees of 0.3–0.7, a stable phase of char gasification is reached. The presentation of the following experiments will be scaled to show only this part of the conversion. The last part of the cycle often reaches even higher rates of conversion around char conversion degrees of 0.8, but also becomes more fluctuant. This part is believed to be influenced by the soot/carbon stuck on the walls of the reactor or in the filter during fuel introduction.[27] In the very last part of the graph the rate initially drops and then rises to infinity due to the calculation method getting close to division by zero. Thus the last part from a degree of carbon conversion of 0.7–1.0 is also excluded from further illustrations.

Effect of oxygen carrier, fuel type and oxygen carrier to fuel ratio

Figure 6 shows the char gasification rate as a function of the degree of char conversion for the three different oxygen carriers with Mexican petroleum coke as fuel. The fuel conversion rate with the Brazilian manganese ore is five times higher than with ilmenite which is in agreement with the previously reported investigation.[31] The gasification rate using the Mn-oxide oxygen carrier is about 1.5 times higher than ilmenite, but well below the rate of the manganese ore. As can be seen in Figure 6, there is a high reproducibility in the rate data.

Additionally, fuels such as Swedish wood char and a bituminous Colombian coal (El Cerrejon) were also used. Table 4 shows the arithmetic average rate of char conversion for the

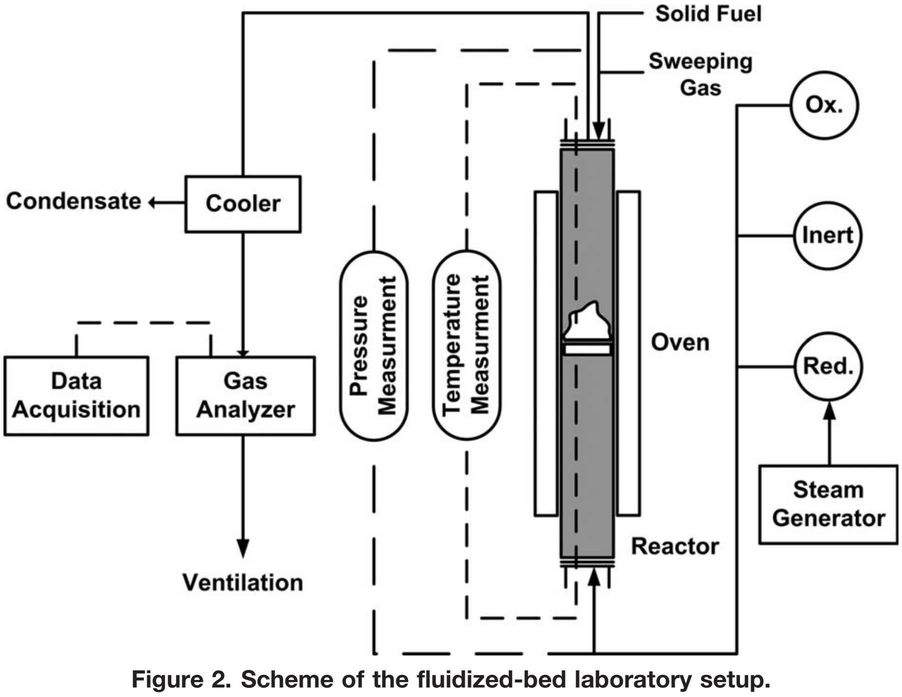

Figure 2. Scheme of the fluidized-bed laboratory setup.

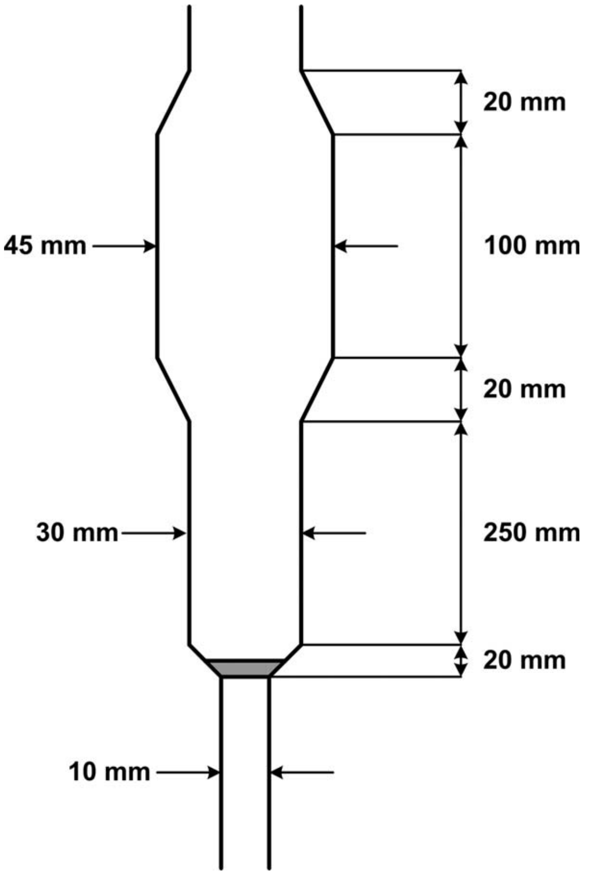

Figure 3. Dimensions of the conical quartz batch reactor.

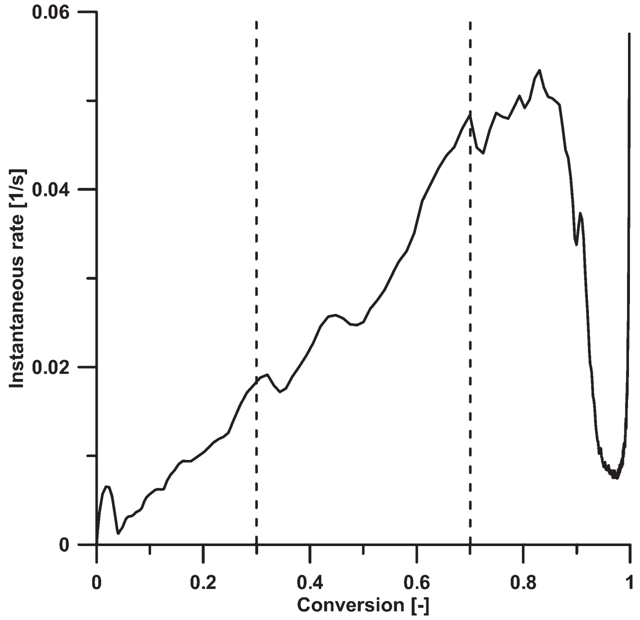

Figure 5. Instantaneous gasification rate r_{inst}, as a function of degree of char conversion, X_C, for manganese ore with petroleum coke as fuel.

different fuels. All fuels show several times higher rate of gasification with the Brazilian manganese ore than with ilmenite or Mn-oxide oxygen carrier. In the case of manganese ore, the Mexican petroleum coke gives a slightly higher char conversion rate than the Colombian coal, while petroleum coke gives a lower rate than the Colombian coal with ilmenite.

In order to investigate the possible influence of H_2 and CO inhibition, their concentrations can be compared for beds of manganese ore, ilmenite and Mn-oxide oxygen carrier in Table 5. The experiments with the manganese ore show higher H_2 and CO concentrations compared to ilmenite and the Mn-oxide oxygen carrier. The experiments with the Mn-oxide particles shows significantly lower H_2 and CO concentrations compared to the other oxygen carriers.

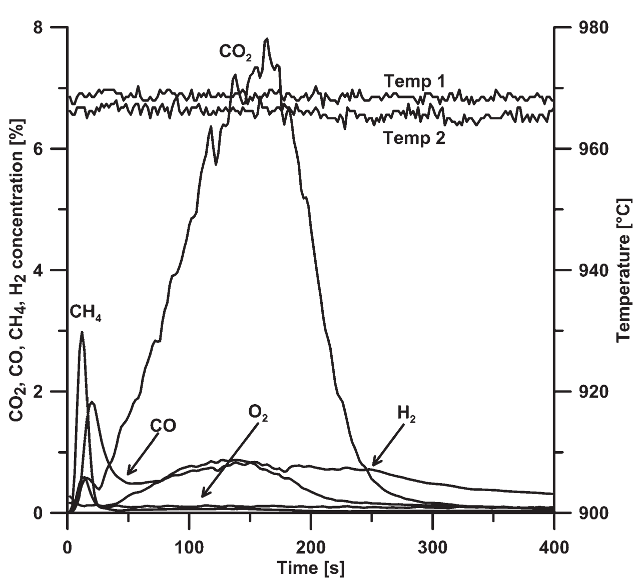

Figure 4. Concentration profiles for a cycle with manganese ore and petroleum coke as fuel.

Gasification is carried out at 970°C with an inlet gas mixture of 50% H_2O in N_2.

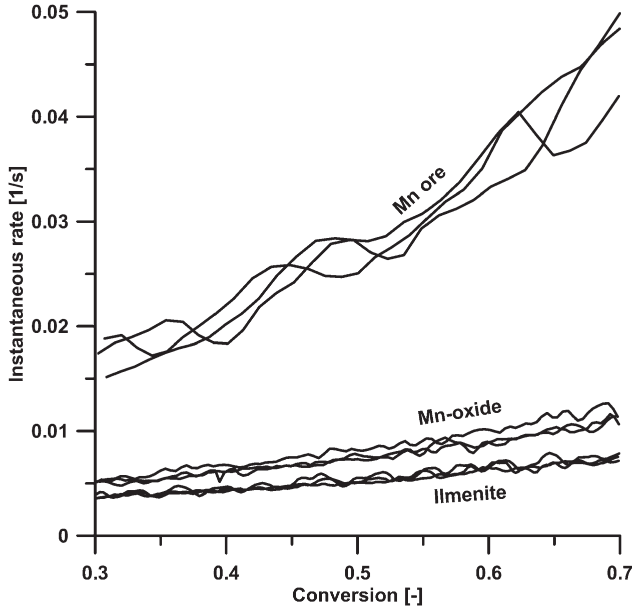

Figure 6. Instantaneous gasification rate r_{inst}, as a function of degree of char conversion, X_C, for manganese ore, Mn-oxide oxygen carrier and ilmenite.

Table 4. Arithmetic Average of the Instantaneous Rate for Different Oxygen Carriers and Fuels

Oxygen Carrier	Manganese ore			Ilmenite			Mn-oxide
Fuel	Petcoke	Wood char	Colombian coal	Petcoke	Wood char	Colombian coal	Petcoke
Average instantaneous rate, $\bar{r}_{inst}$ [1/s]	0.0284	0.0398	0.0253	0.0054	0.0176	0.0107	0.0078

In order to examine the possibility of oxygen release contribution to the rate of gasification from the manganese ore, the oxygen carrier to fuel ratio was varied between 50 and 400. This was done by introducing fuel amounts between 0.05 and 0.4 g to two different bed masses of 20 and 40 g of manganese ore. In Figure 7, the rate of char gasification for each oxygen carrier to fuel mass ratio is shown. It can be observed that the char conversion rate remains roughly constant at 0.025 1/s for oxygen carrier to fuel ratios within feasible borders of experimental conditions. The char conversion rate decreases for very high amounts of fuel possibly due to the ore approaching full reduction.

Effect of mixing of ilmenite and manganese ore

Here, a bed of pure ilmenite was mixed with successively increasing amounts of manganese ore. The amounts were chosen in a way that the influence of very small percentages of manganese ore could be observed. Figure 8 shows the char conversion rate for each experiment as a function of amount of manganese ore in the bed. At the end of the graph, an experiment with the pure manganese ore bed is also included to illustrate the 100% manganese ore case. It can be observed that the gasification rate shows deviation from a linear mixing behavior indicated by a coarsely dashed line. Even small amounts of manganese ore resulted in a significant increase in char conversion and the presence of 10% of manganese ore gave more than a doubling in rate. Since more manganese ore was added to the bed as the experiments proceeded, it should be noted that the total amount of oxygen carrier increases throughout the tests, with exception of the end point of 100% manganese ore.

Figure 9 shows the average H_2 and CO concentrations for the aforementioned described experiments. At low amounts of manganese ore in the bed, the concentration of these gases remains almost constant with H_2 roughly at 0.5% and CO at 0.3%. For the experiment of 100% manganese ore in the bed, the H_2 and CO concentrations are considerably higher, showing values around 0.8%.

Figure 10 shows the gas conversion as a function of amount of manganese ore in the bed. It can be observed that the gas conversion increases with increasing the mass of manganese ore in the bed. This is also in agreement with the results in the 10 kW CLC unit,[30] where gas conversion was significantly improved with the manganese ore as compared to ilmenite.

Discussion

The rate of char conversion for petroleum coke and for Brazilian manganese ore oxygen carrier has been reported as five times faster compared to ilmenite.[30,31] This is reproduced in this work using different solid fuels as shown in Table 4. For all solid fuels, manganese ore shows several times higher char conversion rate than ilmenite. This shows that the higher rate of steam gasification for the manganese ore is not associated with a specific fuel. Thus, other possible mechanisms which can account for the higher rate of gasification of the manganese ore are discussed in the following.

Table 5. H_2 and CO Concentrations for Different Oxygen Carriers

	Manganese ore	Ilmenite	Mn-oxide
H_2 [%]	0.770	0.409	0.155
CO [%]	0.789	0.301	0.035

H_2 and CO inhibition

One mechanism for the high reactivity of the manganese ore is the ability to decrease H_2 and CO inhibition. This means that the manganese ore may react faster with H_2 and CO in the reaction zone, thus, decrease the inhibition effect from these gases on the char gasification. However, the experiments here indicate relatively higher H_2 and CO concentrations in the flue gases using manganese ore in comparison with ilmenite as shown in Table 5. The experiments using Mn-oxide oxygen carrier shows H_2 and CO levels close to zero. Established models for the influence of H_2 on the reaction rate predict lower char conversion rates for steam gasification with increasing H_2 concentrations.[25] Similar models are found for CO inhibition in CO_2 gasification.[36] Considering the results presented, this is the case when comparing ilmenite to the Mn-oxide oxygen carrier. However, the very high-char gasification rate of manganese ore does not conform with established H_2 inhibition models.[25] The H_2 concentration in the reactor for the ore would be expected lower than with the other oxygen carriers, but is clearly

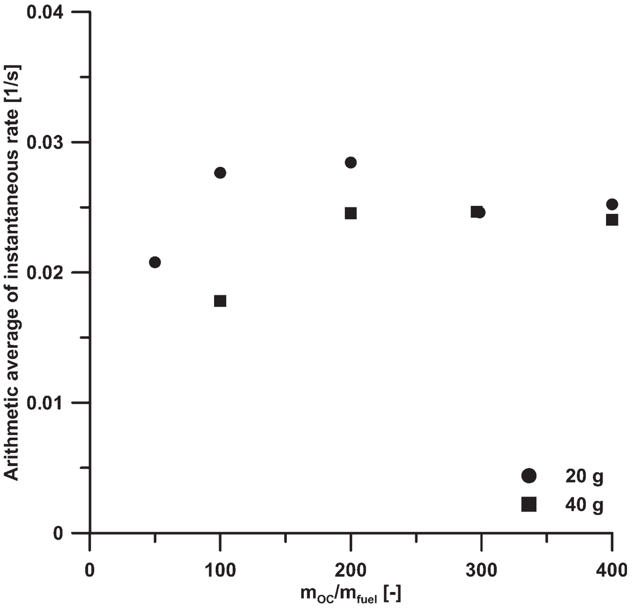

Figure 7. Arithmetic average of instantaneous gasification rate $\bar{r}_{inst}$, as a function of different bed mass to fuel ratios using manganese ore.

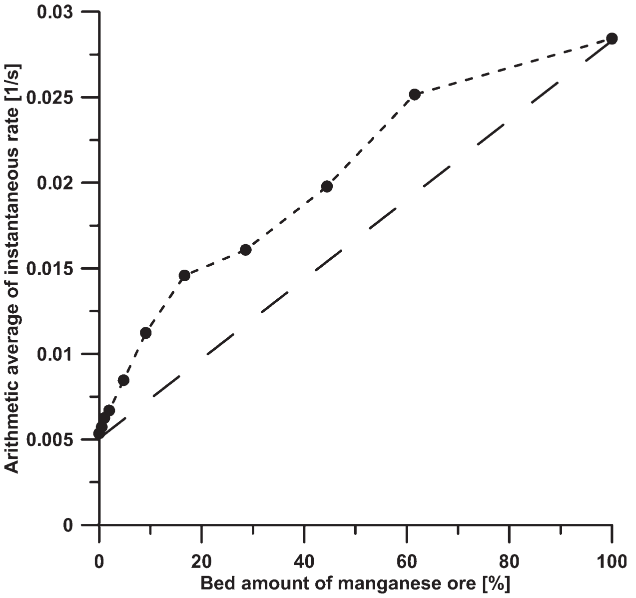

Figure 8. Arithmetic average of instantaneous gasification rate $\bar{r}_{inst}$, as a function of bed mass using manganese ore.

higher. Thus, decrease in H_2 inhibition is unlikely to be the main responsible mechanism.

Oxygen release (CLOU) effect

Low-oxygen concentration levels in the reactor were reported in case of the Brazilian manganese ore and an extremely slow rate of char conversion was seen when the manganese ore was fluidized in 100% N_2.[31] Figure 7 shows an almost constant rate of steam gasification for different ratios of oxygen carrier to fuel. This further corroborates that the Brazilian manganese ore has no significant oxygen uncoupling properties. For typical CLOU materials, the rate of char conversion should increase with the increase of oxygen carrier to fuel ratio. The higher mass of oxygen carrier particles in the reactor releases more oxygen, and, hence, yield faster fuel conversion. Furthermore, this experiment shows that the absolute bed mass of manganese ore has no significant influence on the experimental result within the investigated borders. Therefore, the rapid char conversion when using manganese ore is not likely to be explained by CLOU. Moreover, experiments with a CLOU oxygen carrier should produce only small amounts of H_2 and CO due to higher gas conversion, which is also not the case with the manganese ore as shown in Table 5.

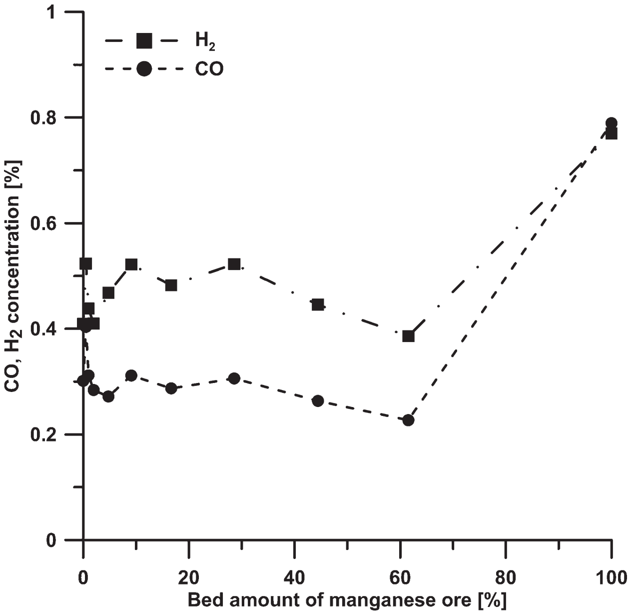

Figure 9. H_2 and CO concentrations during the mixing of ilmenite with manganese ore.

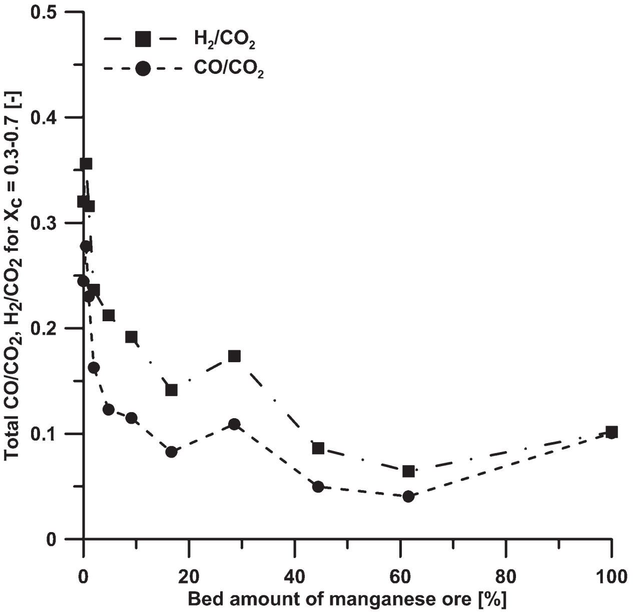

Figure 10. Total H_2/CO_2 and CO/CO_2 ratios during the mixing of ilmenite with manganese ore.

Catalytic effect

To examine the catalytic influence of the manganese ore, the ore particles were introduced to a bed of ilmenite at different mixing ratios between both materials. This was done to investigate the ore's magnitude of influence on the carbon conversion. As shown in Figure 8, even small amounts of manganese ore increase the steam gasification rate significantly which suggests a catalytic influence from the ore.

Initially, Mn_3O_4 as oxygen carrier could be suspected to be responsible for the high rate of char conversion of the ore. However, as shown in Figure 6, the rapid char conversion for the Brazilian manganese ore is not reached by the Mn-oxide oxygen carrier. This suggests that the rapid char conversion for the Brazilian manganese ore does not solely result from Mn_3O_4 itself. Consequently, the results suggest that the higher rate of char gasification in case of the manganese ore could be due to the remaining impurities of the ore. Table 2 shows the elemental analysis of the Brazilian manganese ore. McKee[37] and Haga et al.[38] have shown that alkali and alkaline earth metals can catalyze the carbon steam gasification reaction. The use of K_2CO_3-impregnated iron ore as oxygen carrier in CLC has also shown to increase the rate of steam gasification of an anthracite coal.[39] A review of the possible mechanisms for catalytic gasification can be found in the work by Moulijn et al.[40] It should be noted, however, that the experimental conditions in catalytic gasification are rather different where char is loaded or impregnated with the catalyzing agent and the gasification is carried out at relatively lower temperatures. Thus, the possibility of a contribution from such impurities to the rate of steam gasification of char requires additional studies.

Conclusions

In this work, the reported higher rate of steam gasification when using a Brazilian manganese ore as oxygen carrier compared to ilmenite is further investigated. The results indicate that the higher rate of steam gasification for the manganese ore is not associated with a specific fuel. It is also observed that the measured H_2 concentration when using the manganese ore does not agree with established models for H_2 inhibition. The rate of char gasification for the ore was also compared with a manufactured Mn-oxide oxygen carrier, which showed a much higher reactivity toward H_2, and, thus, lowers H_2 concentration in the bed. Yet the ore was found to give a much higher rate of char gasification. This clearly indicates that the decrease in H_2 inhibition is unlikely to be the main responsible mechanism for the higher rate of char conversion for the manganese ore. The possibility of oxygen release contribution from the manganese ore was also investigated by variation of oxygen carrier to fuel ratio. However, the rate of gasification remained constant and the results indicate little support for oxygen release (CLOU effect) from the ore. The manganese ore was also mixed in different ratios in a bed of ilmenite. The results showed an increase in rate of char conversion even with only a few percentages of the manganese ore particles in the bed. This indicates that a catalytic effect by the manganese ore is possible. It is thus suspected that one of the impurities in the ore is responsible for the higher rate of steam gasification for the manganese ore.

Acknowledgments

This work is based on a master thesis carried out at the division of Environmental Inorganic Chemistry at Chalmers University of Technology. It was examined at the University of Siegen at the chair of Energy and Environmental Process Engineering by Prof. Dr-Ing. habil. Wolfgang Krumm. This work was financed by DAAD (Deutscher Akademischer Austausch Dienst) scholarship and was partly funded by Chalmers University of Technology via the Energy Area of Advance and Statens Energimyndighet, project number: 32368-1.

Literature Cited

1. Pachauri RK, Reisinger A. Fourth Assessment Report: Climate Change (Synthesis Report). Geneva, Switzerland: Intergovernmental Panel on Climate Change; 2007.
2. Herzog HJ. CO2 capture and storage: Costs and market potential. In: Rubin ES, Keith DW, Gilboy CF, Wilson M, Morris T, Gale J, Thambimuthu K, Thambimuthu K, eds. Greenhouse Gas Control Technologies 7. Oxford, UK: Elsevier Science; 2005;21–28.
3. Jerndal E, Mattisson T, Lyngfelt A. Thermal analysis of chemical-looping combustion. *Chem Eng Res Des.* 2006;84:795–806.
4. Lewis KW, Gilliland ER, Sweeney MP. Gasification of carbon metal oxides in a fluidized powder bed. *Chem Eng Prog.* 1951;47:251–256.
5. Ishida M, Jin H. A new advanced power-generation system using chemical-looping combustion. *Energy.* 1994;19:415–422.
6. Lyngfelt A, Leckner B, Mattisson T. A fluidized-bed combustion process with inherent CO_2 separation; application of chemical-looping combustion. *Chem Eng Sci.* 2001;56:3101–3113.
7. Lyngfelt A, Thunman H, Construction and 100 h of operational experience of a10 kW chemical looping combustor. In: Thomas D, ed. The CO2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations For Climate Change Mitigation. London, UK: Elsevier Science; 2003.
8. Kolbitsch P, Pröll T, Bolhar-Nordenkampf J, Hofbauer H. Design of a chemical looping combustor using a dual circulating fluidized bed (DCFB) reactor system. *Chem Eng Technol.* 2009;32:398–403.
9. Berguerand N, Lyngfelt A. Design and operation of a 10 kW$_{th}$ chemical-looping combustor for solid fuels - testing with South African coal. *Fuel.* 2008;87:2713–2726.
10. Cuadrat A, Abad A, García-Labiano F, Gayán P, de Diego LF, Adánez J. Effect of operating conditions in chemical-looping combustion of coal in a 500 W$_{th}$ unit. *Int J Greenhouse Gas Control.* 2012;6:153–163.
11. Markström P, Lyngfelt A, Linderholm C. Chemical-Looping Combustion in a 100 kW unit for Solid Fuels. In: 21st International Conference on Fluidized Bed Combustion. Naples, Italy; June 3–6, 2012.
12. Lyngfelt A. Oxygen carriers for chemical looping combustion - 4000 h of operational experience. *Oil Gas Sci Technol.* 2011;66:161–172.
13. Lyngfelt A, Mattisson T. Materials for chemical-looping combustion. In: Stolten D, Scherer V, eds. Efficient Carbon Capture for Coal Power Plants. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2011.
14. Hossain MM, de Lasa HI. Chemical-looping combustion (CLC) for inherent CO_2 separations-a review. *Chem Eng Sci.* 2008;63:4433–4451.
15. Adanez J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF. Progress in chemical-looping combustion and reforming technologies. *Progr Energy Combust Sci.* 2012;38:215–282.
16. Scott SA, Dennis JS, Hayhurst AN, Brown T. In situ gasification of a solid fuel and CO_2 separation using chemical looping. *AIChE J.* 2006;52:3325–3328.
17. Mattisson T, Lyngfelt A, Leion H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int J Greenhouse Gas Control.* 2009;3:11–19.
18. Mattisson T, Leion H, Lyngfelt A. Chemical-looping with oxygen uncoupling using CuO/ZrO_2 with petroleum coke. *Fuel.* 2009;88: 683–690.
19. Arjmand M, Azad A-M, Leion H, Lyngfelt A, Mattisson T. Prospects of Al_2O_3 and $MgAl_2O_4$-supported CuO oxygen carriers in chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU). *Energy Fuels.* 2011;25:5493–5502.
20. Leion H, Larring Y, Bakken E, Bredesen R, Mattisson T, Lyngfelt A. Use of $CaMn_{0.875}Ti_{0.125}O_3$ as oxygen carrier in chemical-looping with oxygen uncoupling, *Energy Fuels.* 2009;23:5276–5283.
21. Arjmand M, Hedayati A, Azad A-M, Leion H, Rydén M, Mattisson T. $Ca_xLa_{1-x}Mn_{1-y}M_yO_{3-\delta}$ (M = Mg, Ti, Fe, or Cu) as oxygen carriers for chemical-looping with oxygen uncoupling (CLOU). *Energy Fuels.* 2013. doi:10.1021/ef3020102.
22. Azimi G, Rydén M, Leion H, Mattisson T, Lyngfelt A. $(Mn_zFe_{1-z})_yO_x$ combined oxides as oxygen carrier for chemical-looping with oxygen uncoupling. *AIChE J.* 2012;59:582–588.
23. Azimi G, Leion H, Rydén M, Mattisson T, Lyngfelt A. Investigation of different Mn-Fe oxides as oxygen carrier for chemical-looping with oxygen uncoupling (CLOU). *Energy Fuels.* 2012;27:367–377.
24. Hüttinger KJ, Merdes WF. The carbon-steam reaction at elevated pressure: Formations of product gases and hydrogen inhibitions. *Carbon.* 1992;30:883–894.
25. Keller M, Leion H, Mattisson T, Lyngfelt A. Gasification inhibition in chemical-looping combustion with solid fuels. *Combust Flame.* 2011;158:393–400.
26. Abad A, Mattisson T, Lyngfelt A, Johansson M. The use of iron oxide as oxygen carrier in a chemical-looping reactor. *Fuel.* 2007; 86:1021–1035.
27. Leion H, Mattisson T, Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion. *Fuel.* 2007;86:1947–1958.
28. Leion H, Mattisson T, Lyngfelt A. Use of ores and industrial products as oxygen carriers in chemical-looping combustion. *Energy fuels.* 2009;23:2307–2315.
29. Fossdal A, Bakken E, Øye BA, Schøning C, Kaus I, Mokkelbost T, Larring Y. Study of inexpensive oxygen carriers for chemical looping combustion. *Int J Greenhouse Gas Control.* 2011;5:483–488.
30. Linderholm C, Lyngfelt A, Cuadrat A, Jerndal E. Chemical-looping combustion of solid fuels - Operation in 10 kW unit with two fuels, above-bed and in-bed fuel feed and two oxygen carriers, manganese ore and ilmenite. *Fuel.* 2012;102:808–822.
31. Arjmand M, Leion H, Lyngfelt A, Mattisson T. Use of manganese ore in chemical-looping combustion (CLC) - Effect on steam gasification. *Int J Greenhouse Gas Control.* 2012;8:56–60.

32. Schwebel GL, Leion H, Krumm W. Comparison of natural ilmenites as oxygen carriers in chemical-looping combustion and influence of water gas shift reaction on gas composition. *Chem Eng Res Des.* 2012;1–10.
33. Adánez J, Cuadrat A, Abad A, Gayán P, de Diego LF, García-Labiano F. Ilmenite activation during consecutive redox cycles in chemical-looping combustion. *Energy Fuels.* 2010;24:1402–1413.
34. Zafar Q, Abad A, Mattisson T, Gevert B, Strand M. Reduction and oxidation kinetics of Mn_3O_4/Mg-ZrO_2 oxygen carrier particles for chemical-looping combustion. *Chem Eng Sci.* 2007;62:6556–6567.
35. Leion H, Lyngfelt A, Johansson M, Jerndal E, Mattisson T. The use of ilmenite as an oxygen carrier in chemical-looping combustion. *Chem Eng Res Des.* 2008;86:1017–1026.
36. Brown TA, Dennis JS, Scott SA, Davidson JF, Hayhurst AN. Gasification and chemical-looping combustion of a lignite char in a fluidized bed of iron oxide. *Energy Fuels.* 2010;24:3034–3048.
37. McKee DW. Catalysis of the graphite-water vapor reaction by alkaline earth salts. *Carbon.* 1979;17:419–425.
38. Haga T, Nogi K, Amaya M, Nishiyama Y. Composite catalysts for carbon gasification. *Appl Catal.* 1990;67:189–202.
39. Gu H, Shen L, Xiao J, Zhang S, Song T, Chen D. Iron ore as oxygen carrier improved with potassium for chemical looping combustion of anthracite coal. *Combust Flame.* 2012;159:2480–2490.
40. Moulijn JA, Cerfontain MB, Kapteijn F. Mechanism of the potassium catalysed gasification of carbon in CO_2. *Fuel.* 1984;63:1043–1047.

Manuscript received Oct. 30, 2012, revision received Mar. 31, 2013, and final revision received Jun. 4, 2013.