EXAMINATION OF METHANE CHEMCIAL LOOPING COMBUSTION WITH SELECTED NATURAL Fe-BASED OXYGEN CARRIER IN 10 KW FLUIDIZED BED

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Abstract - the paper shows the results of a chemical looping combustion (clc) study. The clc technology has been significantly developed during the last two decades and nowadays is considered as one of the most promising combustion methods (hossain et al. 2008). The significant advantages of clc are a concentrated pure co_2 stream that may be obtained after water condensation without any energy penalty for its separation. Furthermore, the no_x emissions to the atmosphere from combustion process are highly reduced (fossdal et al. 2011).

The objective of this work is to study the reaction kinetics during both the reduction and oxidation reactions for selected naturally occurring material used as an oxygen carrier (oc). The oc performance is crucial for successful clc power operation such as low cost, availability (leion et al. 2009, ksepko et al. 2014). Therefore, a highly reached in Fe oxide (Ksepko at al. 2016) - Kryvbas ore was selected and evaluated during this study.

The first part of the OC examination relied on the reactivity measurements performed at isothermal conditions (up to 950°C) during multiple redox cycles using a Thermo-Gravimetric Analyzer (TGA). CH_4 was used for reduction while synthetic air was used for the oxidation reactions. The kinetic parameters: activation energy, pre-exponential factor, reaction order were determined for redox reactions. Models of the reactions have been selected by application of the model fitting method.

Since the material showed promising reactivity in CLC reactions during TGA study material therefore further it was applied in higher scale in 10 kW fluidized bed installation in Clean Coal Technology Center, Poland. Realization the experiments as multi cycle CLC tests in 10 kW installation both with pure methane and methane contaminated with H_2S showed that the solid material might be practically used as an oxygen carrier in a real CLC power system in a rush fuel combustion conditions with a suitable combustion efficiency.

INTRODUCTION

The chemical looping combustion concept (CLC) has been shown to be a promising technology for effective CO_2 capture. In the process, oxygen carriers, typically metal oxides, are used for transportation of oxygen to fuel, avoiding contact between air and fuel. This is way is alternative for the direct mixing of fuel and airand was described widely elsewhere (Hossain et al. 2008). The important advantage of using CLC is that a concentrated CO_2 stream is obtained from the combustion gas stream when water condensed without requiring any energy for its separation or purification. Furthermore, the NO_X emissions to the atmosphere from combustion process are highly reduced (Fossdal et al. 2011).

In CLC, the suppliers of the oxygen for fuel conversion are metal oxides or mixtures of various metal oxides and inert materials. Many oxygen carriers (OCs) are known, including copper, manganese, iron, cobalt or nickel oxides used as active materials as well as aluminum, titanium, zirconium oxides which are used as inert materials. A suitable OC in CLC process must: have high reactivity, sufficient oxygen transport capacity, high mechanical strength, sufficient attrition resistivity etc. The OC performance is crucial for successful CLC power operation including low cost, availability (Leion et al. 2009, Ksepko et al. 2014). Therefore, a highly reached in Fe oxide (Ksepko at al. 2016) - Kryvbas ore was selected and evaluated during this study.

EXPERIMENTAL

Thermogravimetric analysis experiments were conducted in a pressurized thermogravimetric analyser HP 150s TA – Rubotherm. In experiments, the weight change of the oxygen carrier samples was measured isothermally as a function of the time during the reduction-oxidation cycles. Five redox cycles at each temperature were conducted, for the determination of stability. A sample of approx. 100 mg was used. A CH_4/CO_2/He gas mixture was used for the reduction reaction. Different methane concentrations were used: 10–25 % with 60% of CO_2. The reason for using CO_2 was to maintain of the reduction of hematite to magnetite phase only, by preventing further reduction to wüstite or metallic Fe (Cabello et al. 2014). For the oxidation 5–20 % of O_2/He gas mixtures were used. To understand the effect of temperature, TGA experiments were performed at 750 °C and 950 °C.

Because the calculations described in this paper do account for the concentration of the gaseous substrate, a kinetic expression for the solid–gas reaction rate can be described by the following equation (1):

$$\frac{dX}{dt} = k' P^n f(X) \tag{1}$$

Where: f*(X)* is a structural factor or a model of the reaction that describes the physical or chemical properties during the reaction

For the calculation of the other kinetic parameters, such as E_a and A_0, the reaction rate constant must be calculated for different temperatures. Then, the activation energy and the pre–exponential factors are calculated from the Arrhenius equation as the slope and intercept of ln*(k)* vs. *1/T*, respectively, based on equation (2):

$$\ln(k) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln(A_0 \cdot P^n) \tag{2}$$

The reaction order with respect to gaseous reagent that is in this paper CH_4 (fuel, reducer) and O_2 (oxidizer) was calculated based on equation (3:

$$\ln(k) = \ln(k') + n \cdot \ln P_g \tag{3}$$

That means that the reaction order with respect to gaseous reactant is calculated from (8) equation as the slope and intercept of *ln(k)* vs. *ln(P)* (eq.3).
The stable fifth redox TGA data were used for the calculations. Mathcad Prime 2.0 software was used for the kinetic parameters calculations.

The 3-10 kW CLC rig in IChPW, presented in Fig. 1, consists of two fluidized bed reactors: fuel (5) and air reactor (8). The oxygen carrier is fed to the fuel reactor (via the screw feeder (4)) where the combustion of fuel occurs. The fuel reactor can be fed by mixture or gases such as: CH_4, H_2, CO, CO_2, N_2, steam, syngas from gasification plant. The reduced oxygen carrier is directed to the air reactor through the loop seal (6), where the oxidation of the oxygen carrier takes place. The air reactor (8) can be fed by mixture or separate gases such as: air, O_2, CO_2, N_2, steam. The both reactors are equipped with heating systems, and works up to 1000°C. The gas mixtures are heated up in gas preheaters (15A, B) (up to 650°C), where also water can be pumped to produce steam. The hot oxidized OC is directed from air reactor (8) through the overflow to the heat-insulated container (3) and then to the mobile container (1). The oxygen carrier is transported to the tank which is coupled with the screw feeder (4) directed OC to the fuel reactor (5) and carry out the next cycle. Outgases from both fuel and air reactor are directed to ceramic filters (9A i B) and then to post-combustion chamber for burn-off of combustible residual gas components. Exhaust gases from the combustion chamber are air-cooled and directed to the chimney. The rig is equipped with on-line analyzers system that enables to continuously monitoring of the composition of the outlet gas from the fuel reactor (CO, CH_4, H_2, CH_4), and from the air reactor (O_2). In addition, exhaust gases might be collected in the gas sampling bags, and the gas composition might be monitored by a GC.

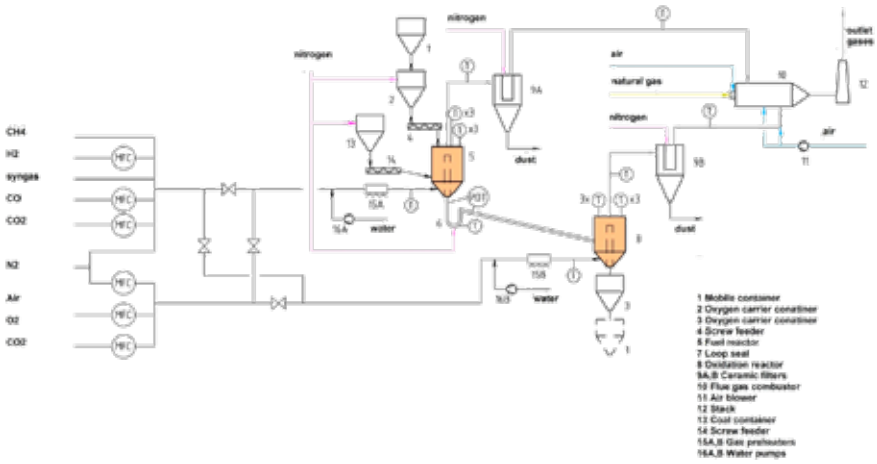


Fig 1. Scheme of CLC rig.

The reactors for study chemical looping combustion processes work in fluidization regime, and therefore the execution of preliminary calculations of the characteristics of the fluidized bed is needed prior any work associated with the combustion of methane in the CLC. The basic parameter which is the linear velocity of the gas in the minimum fluidization condition is essential to test combustion of fuel in the chemical oxide loop.

In the fluidized bed reactor, the gas velocity should be higher than the minimum fluidizing velocity for a given particle diameter. The minimum fluidizing gas velocity can be calculated according to following equation (4):

$$\frac{d_p u_{mf} \rho_g}{\mu_g} = \left(33{,}7^2 + 0{,}0408 \frac{d_p^3 \rho_g (\rho_p - \rho_g) g}{\mu_g^2}\right)^{1/2} - 33{,}7 \qquad (4)$$

The second threshold value is the terminal velocity of the particles. This describes what should be the gas velocity for the particles of a given diameter where entrainment of the particles from the fluid bed is starting. The terminal velocity of the particles is determined by the relation (5):

$$u_t^* = \left[\frac{18}{(d_p^*)^2} + \frac{0.591}{(d_p^*)^{1/2}}\right]^{-1} \qquad (5)$$

where:

$$d_p^* = d_p \left(\frac{\rho_g (\rho_p - \rho_g) g}{\mu_g^2}\right)^{\frac{1}{3}} \qquad (6)$$

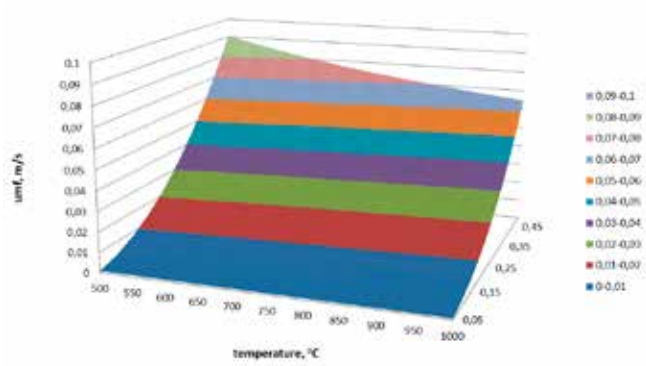
$$u_t^* = u_t \left(\frac{\rho_g^2}{(\rho_p - \rho_g) g \mu_g}\right)^{1/3} (4) \qquad (7)$$

u_g – gas velocity, μ_g – gas viscosity, ρ_g – gas density

The realization of the above-described calculation procedure and simulation code with using of MathCad Prime 2.0 algorithm enabled to estimate the range of gas flow through the fluidized bed reactors.

As shown in Fig. 2, the change in process temperature effects the changes of the fluidized bed properties. According to the below figure gas velocity must be higher than minimum fluidizing velocity and terminal velocity of the particles.

(a)



(b)

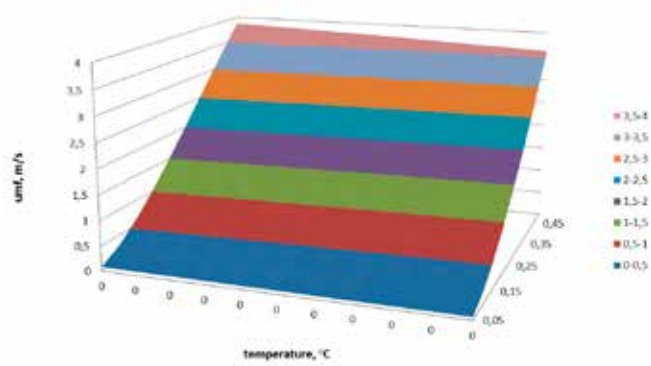


Fig. 2. Minimum fluidization gas velocity vs. temperature and particle diameter (a) and terminal velocity (b).

The process was carried out with the bubbling fluidization regime corresponding to u/u_{mf} = 2-5. In order to perform a mass balance of the process, inlet flows of each gases and their conversion in fuel and oxidation reactors should be estimated. Conversion of the CH_4 and O_2 in the both reactors are calculated by the eq. (8) and (9) respectively:

$$\eta_p = \frac{F_{p,0}^{\cdot} - \dot{F}_p}{F_{p,0}^{\cdot}} \tag{8}$$

$$\eta_{O2} = \frac{F_{O2,0}^{\cdot} - F_{O2}^{\cdot}}{F_{O2,0}^{\cdot}} \tag{9}$$

Where:
η_p – conversion degree of fuel in the fuel reactor, $F_{p,0}^{\cdot}$ – mass stream of CH_4 to fuel reactor, $\dot{F}_p$ – mass stream of CH_4 from fuel reactor, η_{O2} – conversion degree of oxygen in air reactor, $F_{O2,0}^{\cdot}$ – mass stream of O_2 to air reactor, $F_{O2}^{\cdot}$ – mass stream of O_2 from air reactor.

From the point of view of the CLC, the very important parameter is the ratio of the mass flow rate of an oxygen carrier to the mass flow of fuel φ, which is expressed by the relation (10):

$$\phi = \frac{F_{OC}^{\cdot}}{\dot{F}_p} \tag{10}$$

Where: – $F_{OC}^{\cdot}$ – mass flow if oxygen carrier

Since, one of the most important applied parameters for oxygen carrier selection for a CLC power plant is oxygen transport capacity, therefore the oxygen transport capacities were calculated for Fe–based naturally occurring oxygen carrier of 84.86 wt. % Fe_2O_3, 8.55 wt. % SiO_2 and 1.03 wt. % Al_2O_3 material. The theoretically weight changes in accordance to reaction stoichiometry for CH_4 gas reduction of Fe_2O_3 were calculated according to the reactions:
The final total mass balance which expresses the balance of oxygen consumed in the combustion of methane, is shown by equation (11):

$$\frac{3\left(\dot{V_{CH4,0}} - \dot{V_{CH4}}\right)}{\dot{V_{O2,0}} - \dot{V_{O2}}} > 1 \qquad (11)$$

Calculations based on presented relations enables to characterize the Chemical Looping Combustion process. They also enable the calculation of the mass balance for the both individual reactors and the balance of the combustion process.

RESULTS

Kinetic analysis

Continuous Chemical Looping Combustion performance was observed during 10 cycle test at 850°C with using 3% H_2/Ar + steam. Furthermore, the same great behavior was observed for other temperatures (750–950 °C). The theoretical weight change corresponding to reduction of Fe_2O_3 to Fe_3O_4 from Kryvbas ore (where amount of active phase that is Fe_2O_3 is equal to 84.86 wt. %) is 2.83 wt. %. In the reactivity testing, oxygen transport capacities were ~2.8 wt. %. That was achieved since CO_2 stream was added to the fuel. Based on observed masses decreases it may be concluded that the final reduction state for the OC was Fe_3O_4. Therefore, the kinetics data describes the final reduction of Fe_2O_3 to Fe_3O_4. It is important to outline that, Kryvbas ore as a prospective OC does not need an extra handling. In other words it does not need for example activation as it is a case for Ilmenite another natural carrier (den Hoed et al. 2011, Jerndal et al. 2011). Fig. 3 shows the fractional reduction for the high concentrated in Fe natural oxygen carrier, which was calculated for 750-950 °C.

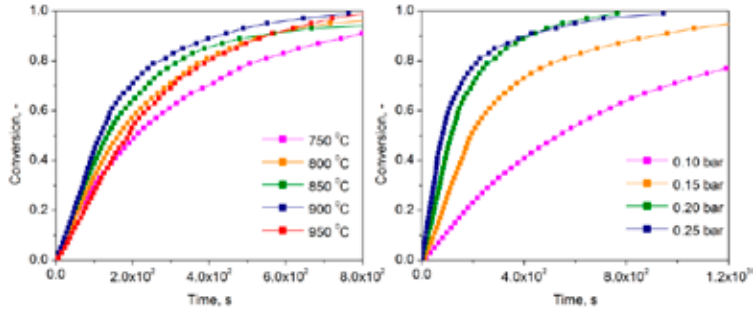


Fig 3. Fractional reduction versus time for Kryvbas ore for different temperature conditions and different reagent (CH_4) concentration conditions.

The positive temperature effect on rate is observed, that is because with the temperature increase the reaction rate increase was observed. In Fig. 3 also fractional reduction versus time for Kryvbas ore for different methane concentration (10, 15, 20 and 25 %) is shown. Here, once more the increase in reduction rate is observed while increasing the reagent concentration.

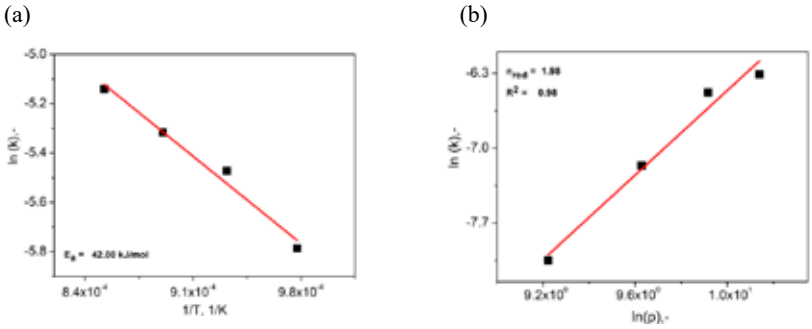


Fig. 4. Arrhenius plot (a) and reduction reaction order determination (b) of the reduction reaction of Krivbas ore.

The calculated reduction reaction parameters for the F1 model are as follows: E_a = 42.0 kJ/mole, R^2 = 0.98 and $A_0 = 9.9 \cdot 10^{-6}$ $s^{-1} \cdot Pa^{-n}$ and are shown as Arrhenius plot of the reduction reaction in Fig. 4. The data from 950 °C was not included into the calculation of E_a because of lower reaction rate. This reduction in reaction rate was caused by likely sintering of the sample during redox cycles. The E_a value of reduction reaction is a little bit higher comparing to E_a of for other Fe–based oxygen carriers reported in literature. That is because for Fe_2O_3/TiO_2 it was stated in to be 33.8 kJ/mole (Ksepko et al. 2014), and also for Fe_2O_3/bentonite that was equal to 29 kJ/mole (Son et al. 2006).

Methane Combustion tests

The examples of the results from methane Chemical Looping Combustion tests are presented in Fig. 5. The Fig. shows the changes of temperature in the both reactors of CLC rig, and also the changes in concentrations of gas components behind fluidized bed reactors are shown. Temperature T1 – T6 correspond to the height of the reactor for each 10 cm high.

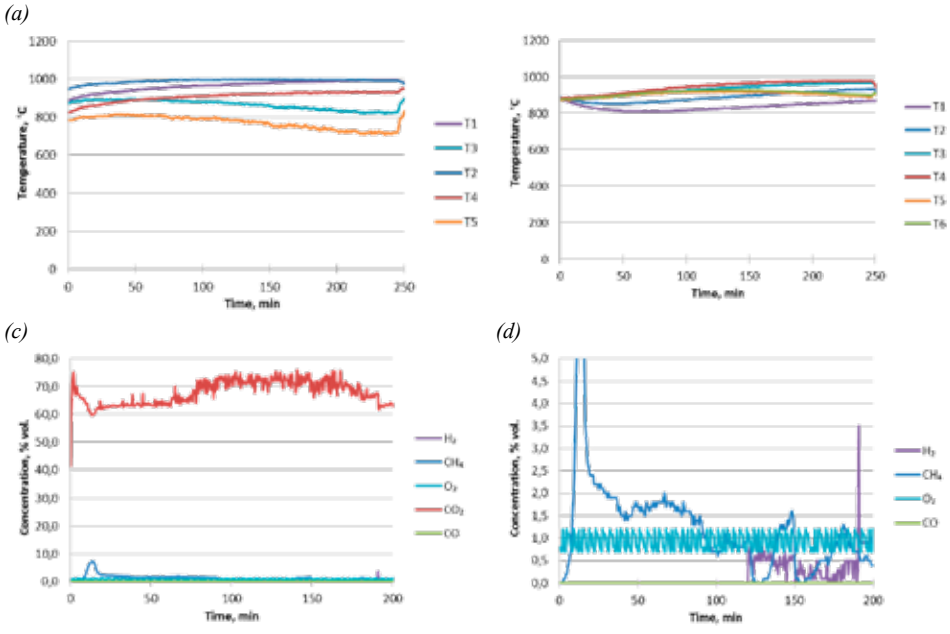


Fig. 5. Graphs of the temperature in the fuel reactor (a) in the air reactor (b), the concentrations of the gaseous components from the fuel reactor (c) the concentrations of the gaseous components from the air reactor (d).

While Tab. 1 summarizes the process parameters of the individual tests for CH_4 combustion. The total number of cycles for oxygen carrier is estimated to be approx. 40.

Tab. 1 Summary of the process parameters for the individual methane combustion tests in Chemical Looping Combustion process (FR – fuel reactor, AR – air reactor)

	Test no.		*1*	*2*	*3*	*4*	*5*	*6*
FR	CH_4	Nm^3/h	0.325	0.325	0.325	0.413	0.300	0.300
	H_2S	ppm	-	-	-	-	1000	1000
	N_2	Nm^3/h	0.350	0.350	0.400	0.400	0.400	0.400
	CO_2	Nm^3/h	1.975	1.975	1.975	2.038	1.900	1.800
	Total gas flow	Nm^3/h	2.650	2.650	2.700	2.850	2.600	2.500
AR	Air	Nm^3/h	3.600	3.600	3.000	4.000	3.300	3.300
	OC/CH_4 ratio	-	1.54	1.45	1.51	1.29	1.42	1.42
	Combustion efficiency	-	0.957	0.968	0.923	0.839	0.842	0.828

As it can be seen, the combustion efficiency decreased with increasing number of the cycles. The ratio of the amount of oxygen carrier to the gas amount was ranging from 1.29 to 1.54 of stoichiometric value. The last redox cycles were carried out with addition of H_2S to the fuel (approx. 1000 ppm in the inlet gas to the fuel reactor). This studies have shown that H_2S was completely oxidized to SO_2 and it was transferred by the oxygen carrier to the air reactor through the loop seal (emissions from the two reactors are comparable, although H_2S was fed only into the fuel reactor).
After the carrying out the CH_4 combustion tests, the impact of CLC process on oxygen carrier characteristics was investigated. The particle size distribution was examined with PSD analyzer, and the reactivity of OC with realized by using of TGA instrument. Those results are presented in Tab. 2 and Fig. 6.

Tab. 2. PSD and porosity.

		Raw oxygen carrier	Used oxygen carrier
PSD	d (0,1), µm	34.8	138.7
	d (0,5), µm	190.3	233.5
	d (0,9), µm	356.9	383.6
Porosity	%	33.84	27.23

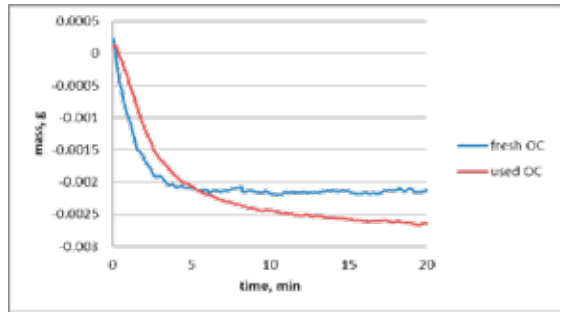


Fig. 6. Reactivity of fresh and reacted oxygen carrier tested at 900 °C.

Based on the obtained results it can be concluded that the oxygen carrier properties have been changed. The porosity of OC was reduced (from 33.84% to 27.23%), and also slightly its reactivity decreased, which is shown in Fig. 6. However, the average particle diameter increased from 190.3 to 233.5 µm, which could be the result of entrainment of particles with the lowest diameter.

CONCLUSIONS

As a result of realized research the opportunity of using low cost iron oxide based ore - Kryvbas ore for the methane combustion in chemical looping process was confirmed. In this study, the kinetics of the reduction and oxidation reactions, for naturally occurring Fe– based oxygen carrier were examined. In total approximately 40 cycles of reduction and oxidation confirming combustion efficiency above 80% were performed. It was concluded that the influence of the impurities presence in the fuel gas (for example hydrogen sulfide - H_2S) in inlet to the fuel reactor have not negatively decreased the combustion efficiency. However, H_2S was oxidized to SO_2, resulting in its emission from the two fluidized bed reactors (air and fuel reactor). The Fe-based oxygen carrier after carrying out 40 redox cycles did not lost significantly its redox properties, which was confirmed by additional TGA studies.

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