RNI: MAHENG/2016/68030

Vol.1 No.6 November-December (2016): 47-58

MGM's JAWAHARLAL NEHRU ENGINEERING COLLEGE

VISTA INTERNATIONAL JOURNAL ON ENERGY, ENVIRONMENT & ENGINEERING

VISTA

Evaluation of Performance of Oxygen Carrier Metal oxides in Chemical Looping Combustion of Coal with Available Resource

S. Y. Guhe[1]*, R. S.K. Monga[1] and Ganesh Kale[2]

Department of Chemical Engineering

MGM's Jawaharlal Nehru Engineering College, Aurangabad

Mahatma Gandhi Mission (MGM), N-6, CIDCO, Aurangabad - 431003, Maharashtra, INDIA

[2]*CSIR-National Environmental Engineering Research Institute, Nagpur, India.*

***Corresponding Author:** E-mail: sadanandguhe@jnec.ac.in Tel.: +91 240 2482893 , Fax:+91 240 2482232

ABSTRACT

Chemical looping combustion (CLC) is a new area of research for clean energy generation from coal. Although the process has advantages of extracting thermal energy with pure CO_2 stream for sequestration, several problems are reported making the technology development slow e.g. development of novel oxygen carrier materials and high temperature in reactor systems. This proposed work is aimed at developing a CLC process system using available oxygen carrier materials and commercially available catalysts that are easy to operate and can demonstrate the underlying phenomena. Studies presented here are based on optimum operating parameters of a fixed bed system which have been obtained by thermodynamic modeling.

Keywords: *Activated charcoal, clean energy; chemical looping combustion; clean coal technology*

1. Introduction

Global warming and climate change are linked to the increasing concentration of the greenhouse gas Carbon dioxide (CO_2) in the atmosphere. Over the last few years, combustion of fossil fuels for power generation has been questioned because of the associated emissions of carbon dioxide and its detrimental effects on environment. Hence, it is necessary to reduce these emissions in order to preserve public acceptance for this type of power generation. Additionally, the consumption of fossil fuels is predicted to increase further in the coming decades, particularly due to the rapid development of populous countries such as India and China. Therefore, it is imperative to develop and implement processes that avoid the emission of anthropogenic CO_2 as per Imtiaz *et al* [1]. The increasing demands for energy and concern of global warming are inter-twined issues of critical importance. With the pressing need for clean, efficient, and cost-effective energy conversion processes, the chemical looping combustion strategy has evolved as a promising alternative to the traditional carbonaceous fuel conversion processes. Chemical looping processes utilize oxygen carrier particles to indirectly convert carbonaceous fuels while capturing CO_2 for sequestration and/or utilization as mentioned by Tong *et al* [2].

Chemical looping combustion (CLC) is a novel combustion technology with inherent separation of CO_2. Extensive research has been performed on CLC in the last decade with respect to oxygen carrier development, reaction kinetics, reactor design, system

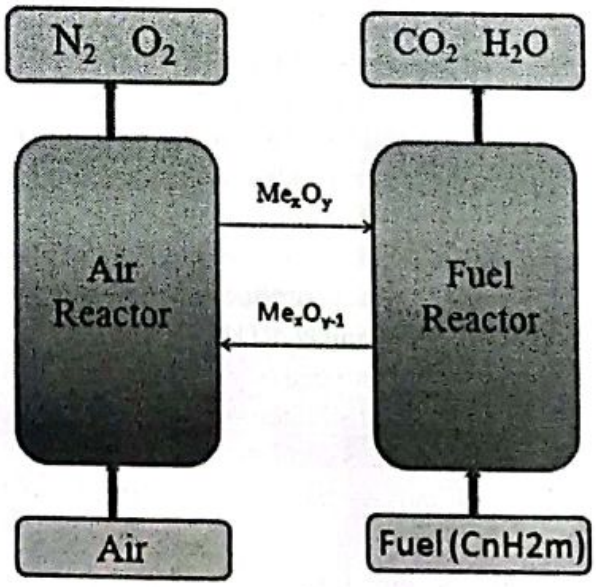

Fig. 1 Chemical-looping Combustion

efficiencies, and prototype testing. Transition metal oxides, such as Ni, Fe, Cu, and Mn oxides, have been reported as reactive species in the oxygen carrier particles as reported by Fang *et al* [3].

The main principle of chemical-looping combustion is based on two separated reactors, an air and a fuel reactor as shown in Fig. 1. Here, combustion oxygen is transferred from the combustion air to the gaseous fuel by means of an oxygen carrier. The fuel and the combustion air are never mixed, and the gases from the oxidation of the fuel, CO_2 and H_2O, leave the system as a separate stream. The H_2O can easily be removed by condensation and pure CO_2 is obtained without any loss of energy for separation reported by Lyngfelt *et al* [4]. Between these two reactors oxygen is transported by an oxygen carrier, which most often is a metal oxide. This arrangement prevents mixing of N_2 from the air with CO_2 from the combustion. The combustion gases consist almost entirely of CO_2 and H_2O. Therefore, the technique reduces the energy penalty that normally arises from the separation of CO_2 from other flue gases, hence, CLC may make capture of CO_2 cheaper as per Leion *et al* [5].

Use of various oxygen carriers in CLC has been investigated by number of workers. Saha *et al* [6] investigated CLC with respect to size of hematite particles as oxygen carrier with respect to temperature over five multiple re-dox cycles under CO_2 gasification environment. Bao *et al* [7] studied reactivity of oxygen carriers related to segregation effect and corresponding CO conversion. Sundqvist *et al* [8] tested the effect of SO_2 on oxygen carrier and proposed that SO_2 had a negative effect on the reactivity of the oxygen carrier because of formation of $CaSO_4$. Cormos *et al* [9] evaluated pre- and post-combustion capture based on various chemical looping options to increase carbon capture and proposed that hydrogen and power co-generation as potential way to increase energy efficiency of coal gasification plants. It was suggested by Quadrat *et al* [10] that CLC technology with solid fuels can lead to energy production with high CO_2 capture efficiencies. Wang *et al* [11] studied the kinetics of catalytic reaction between oxygen carrier NiO with CH_4, H_2, and CO in a fluidized bed reactor. Ryu *et al* [12] investigated Syngas combustion characteristics of various oxygen carrier particles in a fluidized bed reactor and showed that inherent CO_2 separation, NOx-free combustion, and long-term operation without reactivity decay of oxygen carrier particles are possible. Zheng *et al* [13] also investigated the reduction characteristics of Cu-based oxygen carrier with H_2, CO and CH_4 but using a fixed bed reactor. Sharma *et al* [14] recommended use of methane as a fuel and Iron oxide-based oxygen carriers because of its non-toxic nature, low-cost, and wide availability. They pointed out that the residence time of bed material in the air and fuel reactor reduces with increase in the temperature of the air reactor. Mattisson *et al* [15] investigated the feasibility of using NiO as an oxygen carrier, with CH_4 as fuel and in the temperature range 700–1200°C during chemical-looping combustion and suggested that with increase in temperature the yield decreases. Carbon deposition is not expected as long as sufficient metal oxide is supplied to the fuel reactor. Luo *et al* [16] carried out an experimental investigation into direct CLC using coal and biomass with CuO as oxygen carrier and proved that CuO-based oxygen carrier are suitable for CLC of solid fuels. Azimi *et al* [17] carried out experiments in a batch fluidized bed reactor using oxygen carrier particles of Mn and Fe. It was found that OC particles readily release gas phase oxygen at 850°C, and was capable to oxidize CH_4 completely and also convert wood char rapidly to CO_2 during. The particles were able to release oxygen corresponding to more than 3% of their mass in less than 40 seconds. Linderholm *et al* [18] evaluated the performance of spray-dried nickel-based oxygen-carrier particles with a methane as fuel and showed that stable operation and better fuel conversion can be attained by using mixtures of two or three different oxygen-carrier particles. Kempegowda *et al* [19] carried out thermodynamic analysis of gasification of biomass using air, steam, and mixed air/steam for determination of the optimum conditions that can maximize the yield of hydrogen rich gas with low energy consumption.

In this research work, evaluation of performance of three different oxygen carrier metal oxides viz. NiO (25%), CuO (97%), and NiO (65%) in chemical looping combustion of coal with available resources is carried out through experimental investigations. A fixed bed reactor has been used to carry out CLC and thermal stability of these oxygen carrier metal oxides has also been verified through number of experimental runs to check how long these particles can sustain the reduction-oxidation cycles which will decide the effectiveness of these materials.

2. Experimental Work

2.1 Chemical Reaction

Compared to normal combustion, in CLC the fuel is not burnt in air, instead the oxygen carrier supplies the necessary oxygen for conversion of the fuel. The carrier is then re-oxidized 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 ideally consist 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. The occurring reactions are as follows:

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

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

By combining the reduction reaction given by reaction (1) with the oxidation reaction given by reaction (2), the resulting 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.

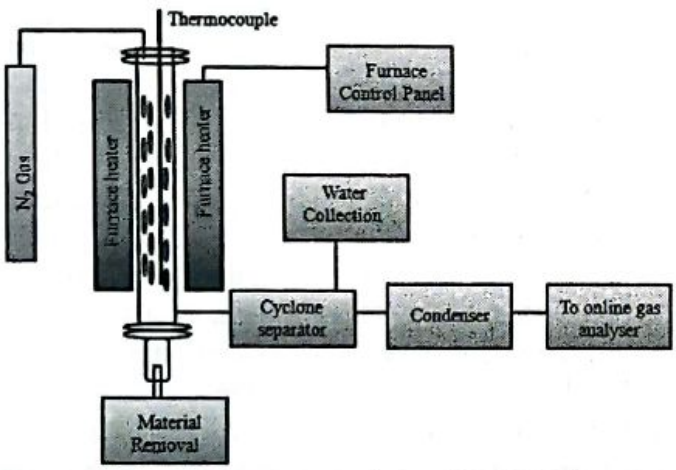

Fig. 2. Schematic representation of fixed bed reactor

2.2 Experimental Setup

A fixed bed reactor is used for redox operation of chemical looping combustion, schematically shown in Fig. 2, whereas Fig. 3 shows actual experimental set-up of fluidised bed rector being used in this proposed work. Three different easily available oxygen carrier materials C-11NK (NiO=25%), CuO (97%) and Ni on silica/alumina (NiO=65%) have been selected to carry out this work. Nitrogen gas (99%) is used for flushing purpose, Oxygen gas (99%) is used for regeneration purpose, Air from compressor for regeneration purpose, Hydrogen gas (99%) is used for reaction with metal oxide.

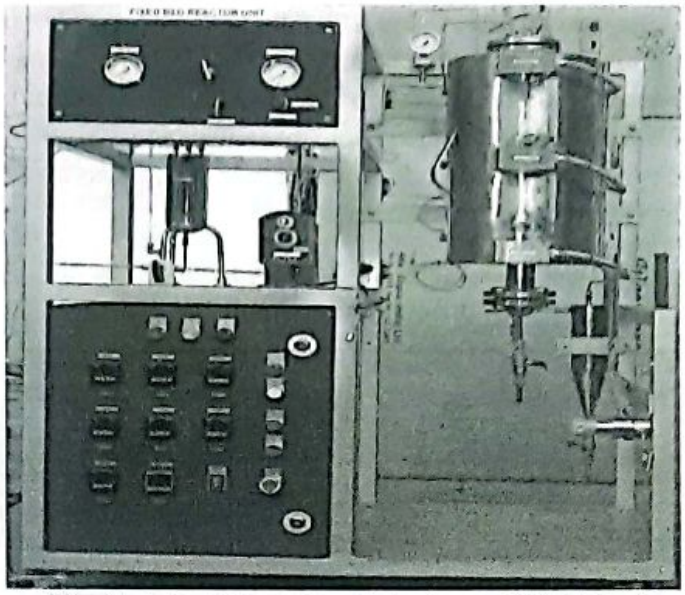

Fig. 3. Actual Experimental set-up of fixed bed reactor.

2.3 Process description

In this work numbers of runs were performed using Hydrogen gas (99%) as a fuel. For each run, collected water value is compared with theoretical value of water expected for each oxygen carrier. The main oxygen carriers used are C-11NK NiO (25%), CuO (97%) and Ni on silica/alumina (65%). For runs using C-11NK NiO (25%), 200g of C-11 NK containing 25% NiO was taken in the fixed bed reactor. The entire system was flushed with nitrogen for 15 minutes to remove all the oxygen present in it followed by hydrogen through the system at a fixed flowrate for respective oxygen carrier. Reaction is carried out at fixed temperature and time. Hydrogen oxidizes to water due to metal oxide and this water generated is collected through the cyclone separator. For regeneration purpose oxygen is passed through the system for different time interval to re-oxidize the metal oxide. After completion of the reaction, fixed bed reactor is flushed again by nitrogen to remove all hydrogen present in a system.

3. Results and discussion

Prior to experimental work, thermodynamic modelling and analysis is carried out to determine the optimum reaction parameters, using thermodynamic equilibrium, mainly temperature and amount of oxygen carrier which has been reported by Monga *et al* [20] and based on those values experimental runs have been carried out in this work.

After flushing the system with nitrogen for 15 minutes to remove all the oxygen from the system, the hydrogen is passed through the system at a Flowrate of 30 ml/min. Data in Table 1 is for Run no. 1 and 2 in which 200 gm of oxygen carrier C-11NK containing 25% NiO was taken in the fixed bed reactor.

Table 1: C-11NK (25% NiO) metal oxide at different temperature

Run no.	Temp (°C)	Time (hr)	Quantity of water		Re-oxidizing medium	Oxidation Duration (hr)	Temp. exotherm
			obtained (ml)	expected (ml)			
1	500	4	6.7	12	Air	10	Not observed
2	600	4	7	12	Air	10	Not observed

In run 1and 2 the system is maintained at 500°C and 600°C respectively for 4 hours (reaction time is kept constant). After 4 hours the system is again flushed with nitrogen for 15 minutes to remove all the hydrogen present inside the reactor. For regeneration purpose air is passed through the system to re-oxidize the metal oxide for 10 hours.

Table 2 shows Data for Run nos. 3, 4, 5, 6, 7, 8, 9 and 10. In this case 500g of CuO 97% was taken in the fixed bed reactor and after flushing with nitrogen, hydrogen is passed through the system at a Flowrate of 80 ml/min. Amongst runs 3, 4, 5 the temperature of system is varied at 500°C, 600°C and 700°C respectively. Whereas for runs 6, 7, 8 the temperature of the reactor is maintained constant at 500°C, while the duration of oxidation varied from 1 to 3 hours but in case of run 8, oxidation was maintained at 500°C. During runs 9 and 10 the temperature of system is maintained constant at 500°C but the oxidation was maintained at 600°C. Water generated due to CuO, has been collected and compared to theoretical value of water expected. In all these experimental runs the system is maintained at respective temperatures for 4 hours (reaction time is kept constant). After 4 hours the system is again flushed with nitrogen for 15 minutes to remove all the hydrogen. For regeneration purpose air is passed through the system to re-oxidize the metal oxide for 1 to 5 hours to see the extent of oxidation in terms of quantity of water obtained.

Table 2. CuO (97%) metal oxide at different temperature

Run no.	Temp (°C)	Time (hr)	Quantity of water		Re-oxidizing medium	Oxidation Duration (hr)	Temp. exotherm (°C)
			obtained (ml)	expected (ml)			
3	500	4	90	110	Oxygen	1	494-577
4	600	4	70	110	Oxygen	1	545-625
5	700	4	40	110	Oxygen	1	560-619
6	500	4	30	110	Oxygen	3	478-534
7	500	4	25	110	Oxygen	3	489-555
8	500	4	22	110	Oxygen	3	443-505
9	500	4	20	110	Oxygen	5	495-550
10	500	4	28	110	Oxygen	5	490-530

Table 3 gives data for Runs 11, 12, 13, 14, and 15. Here, 100g of Ni on silica/alumina 65% was taken in the fixed bed reactor. The entire system was flushed with nitrogen for 15 minutes to remove all the oxygen from the system, followed by hydrogen inlet to the system at a Flowrate of 80 ml/min. In all these runs the temperature was maintained constant at 600°C for 3 hours. After 3 hours of reduction the system is again flushed with nitrogen for 15 minutes to remove all the hydrogen followed by regeneration or re-oxidization of metal oxide by air for 10 hours.

Table 3. NiO (65%) metal oxide at constant temperature

Run no.	Temp (°C)	Time (hr)	Quantity of water		Re-oxidizing medium	Oxidation Duration (hr)	Temp. exotherm (°C)
			obtained (ml)	expected (ml)			
11	600	3	17	15.66	Air	10	Not observed
12	600	3	13	15.66	Air	10	631-662
13	600	3	10	15.66	Air	10	Not observed
14	600	3	7	15.66	Air	10	602-611
15	600	3	5	15.66	Air	10	612-621

Table 1, 2 and 3 gives summary of experimental runs showing various reaction parameters for metal oxide oxygen carriers namely C-11 NK (NiO 25%), CuO (95%) and Ni on Silica/Alumina respectively. In all runs the metal oxides, oxidizes the hydrogen and converts it into water. These Tables also show quantity of water collected due to reaction and expected theoretical value of quantity of water. In the runs from 3 to 9, the water yield decreases compared to runs 1 and 2. But in case of run 10, the water yield has increased. In runs from 11 to 15, the water yield decreases. In all the cases mentioned above except case 2 and 10 water yield decreases, the main reason for decrease in water quantity has been incomplete oxidation of metal oxide which in turn results into lesser reduction of hydrogen and consequently decreased in water yield. The increase in water yield for case 2 and 10 is mainly because of proper oxidation of metal oxides.

Fig. 4 shows the abstract representation of various runs in terms of quantity of water obtained in number of runs as per Table 1,2 and 3. It can be seen that maximum water is

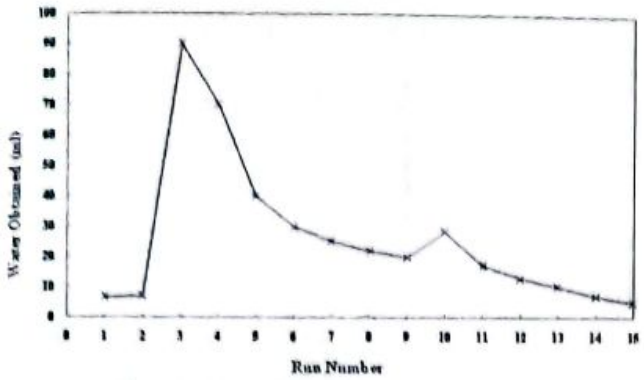

Fig. 4. Quantity of water obtained

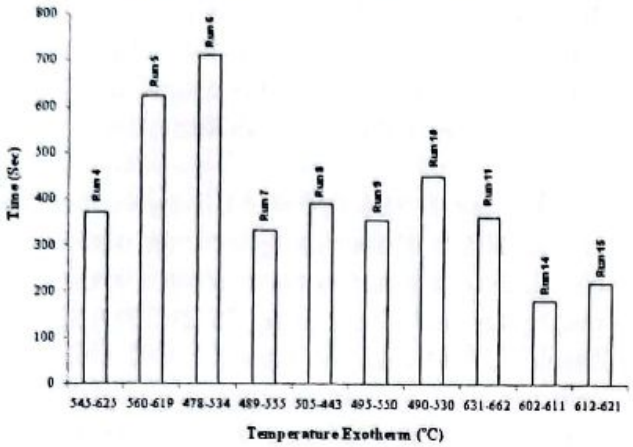

Fig. 5. Temperature Exotherm (metal oxides)

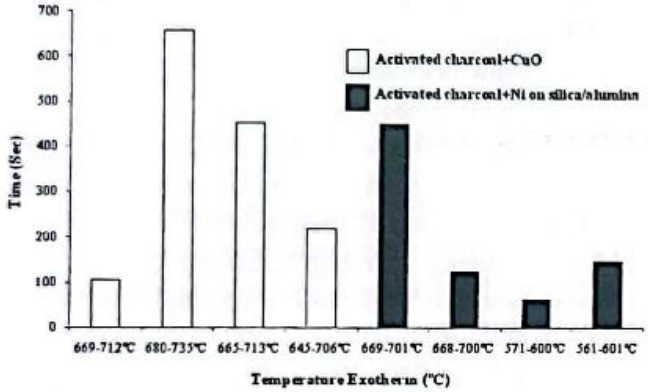

Figure 6: Temperature Exotherm (Activated charcoal + Metal oxide)

obtained in runs 3 to 10 which indicates that CuO (97%) as an metal oxide oxygen carrier material should be preferred over other two materials viz. C-11NK (25% NiO) and NiO (65%) tested in this work. However, Fig. 5 shows the temperature exotherms, for various runs where exotherms have actually been observed, and the corresponding time duration that is observed which clearly indicates the oxidation reaction taking place. Furthermore, reaction of metal oxide with coal is investigated. In this particular case weighed quantity of metal-oxide (CuO and Ni on silica and alumina) is mixed with weighed quantity of activated charcoal and placed at the centre of reactor where they are exposed to high temperature.

The CO_2 concentration goes on increasing and reaches the maximum value and again comes back to 0% which indicates that the complete carbon is consumed. Once the CO_2 percentage in the stream reaches zero, air is passed through the reactor for regeneration of metal-oxide and the temperature exotherms are recorded and are shown in Fig. 6. Table 4 shows various oxygen carrier metal oxides used in this work and their state before and after the reaction.

Table 4. Various metal oxides used and its state before and after the reaction

Metal oxide used	Before use	After use
C-11 NK (NiO=25%)		
CuO (95%)		
Ni on silica/alumina (65%)		

4. Conclusions

Although plenty of work has been reported in the literature based on use of metal oxides as oxygen carriers in CLC process, an attempt has been made to investigate the use of commonly available metal oxide catalysts as an Oxygen carrier. Effect of various reaction parameters and the effect of quantity of these materials have also been investigated. Experimental work has been carried out using three different metal oxides (NiO (25%), CuO (97%), and NiO (65%)). It has been noted that for a metal oxide to be thermally stable, it should sustain for 4-5 reduction-oxidation cycles. It has also been found that CuO (97%) and NiO (65%) showed better results as an Oxygen carriers as they convince the above condition of recycling. On the other hand, NiO (25%) showed meager results as the metal-oxide and could not sustain 4 to 5 cycles. Exotherms have also been studied in case of metal oxides and metal oxides mixed with activated charcoal to understand the extent of reaction. Therefore, it is

recommended to use CuO (97%) over NiO (65%) as former oxygen carrier metal oxide shows better results than later. Also these oxygen carriers are readily available in the market and it saves the procedure and expenses for synthesizing rather new catalyst as an oxygen carrier.

Acknowledgement

This research work is a collaborative project with CSIR's National Environmental Engineering Research Institute (NEERI), Nagpur. Authors would like to express sincere thanks to NEERI for providing the experimental set up to carry out the work.

References

[1] Imtiaz Q, Hosseini D, Müller C.R, Review of Oxygen Carriers for Chemical Looping with Oxygen Uncoupling (CLOU): Thermody-namics, Material Development and Synthesis, Energy Tech. 1 (11) (2013) 633–647.

[2] Tong A, Bayham S, Kathe M.V, Zeng L, Luo S, Fan L.S, Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio State University, App. Energy, 113 (2014) 1836-1845.

[3] Fang H, Haibin L, Zengli Z, Advancements in Development of Chemical Looping Combustion: A Review, Int. J. of Chem. Eng., 2009 (2009) Article ID 710515.

[4] Lyngfelt A, Leckner B, Mattisson T, A fluidized-bed combustion process with inherent CO_2 separation; application of chemical-looping combustion, Chem. Eng. Sci., 56 (10) (2001) 3101-3113,.

[5] Leion H, Jerndal E, Steenari B.M, Hermansson S, Israelsson M, Jansson E, Johnsson M, Thunberg R, Vadenbo A, Mattisson T, Lyngfelt A, Solid fuels in chemical-looping combustion using oxide scale and unprocessed iron ore as oxygen carriers, Fuel, 88 (10) (2009) 1945-1954.

[6] Saha C, Bhattachrya S, Experimental investigation of fluidized bed chemical looping combustion of Victorian brown coal using hematite", Journal of Environmental Chemical Engineering, 2 (3) (2014) 1642-1654.

[7] Bao J, Li Z, Cai N, Experiments of char particle segregation effect on the gas conversion behavior in the fuel reactor for chemical looping combustion, App. Energy, 113 (2014) 1874-1882.

[8] [Sun Sundqvist S, Leion H, Ryden M, Lyngfelt A, Mattisson T, $CaMn_{0.875}Ti_{0.125}O_3$"ä as an Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling (CLOU) Solid-Fuel Testing and Sulfur Interaction", Energy Tech., 1 (5-6) (2013).338-344.

[9] Cormos C, Cormos A, Petrescu L, Assessment of chemical looping-based conceptual designs for high efficient hydrogen and power co-generation applied to gasification processes, Chem. Eng. Res. & Des., 92 (4) (2014) 741-751.

[10]Cuadrat A, Abad A, García-Labiano F, Gayan P, de Diego L F, Adanez J, Ilmenite as oxygen carrier in a chemical looping combustion system with coal, Energy Procedia, 4 (2011) 362-369.

[11]Wang B, Yan R, Zheng Y, Zhao H, Zheng C, Simulated investigation of chemical looping combustion with coal-derived syngas and CaSO4 oxygen carrier, J. Fuel Chem.& Tech., 39 (4) (2011) 251- 257.

[12] Ryu H, Shun D, Bae D, Park M, Syngas combustion characteristics of four oxygen carrier particles for chemical-looping combustion in a batch fluidized bed reactor, Korean J. Chem. Engg., 26 (2) (2009) 523-527.

[13]Zheng X, Su Q, Mi W, Zhang P, Effect of steam reforming on methane-fueled chemical looping combustion with Cu-based oxygen carrier, Int. J. Hydrogen Energy, 39 (17) (2014) 9158-9168.

[14]Sharma R, Chandel M, Delebarre A, Alappat B, 200-MW chemical looping combustion based thermal power plant for clean power generation, Int. J. Energy Res., 37 (1) (2013) 49–58.

[15]Mattisson T, Johansson M, Lyngfelt A, The use of NiO as an oxygen carrier in chemical-looping combustion, Fuel, 85 (5–6) (2006) 736-747.

[16] Luo M, Wang S, Wang L, Lu M, Qian L, Fu H, Experimental investigation of co-combustion of coal and biomass using chemical looping technology, Fuel Proc. & Tech., 110 (2013) 258-267.

[17]Azimi G, Ryden 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., 59 (2) (2013) 582–588.

[18]Linderholm C, Jerndal E, Mattisson T, Lyngfelt A, Investigation of NiO-based mixed oxides in a 300-W chemical-looping combustor, Chem. Eng. Res. & Des., 88 (5–6) (2010) 661-672.

[19]Kempegowda R, Assabumrungrat S, Thermodynamic Analysis for Gasification of Thailand Rice Husk with Air, Steam, and Mixed Air/Steam for Hydrogen-Rich Gas Production, Int. J. Chem. Reac. Engg., 8 (2010) 1-25.

[20]Monga R, Kale G, Guhe S Y, Chemical looping combustion of rice husk, Int. J. Eng. Res. Appl., 5 (5) (2015) 132-138.