



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Combustion and reforming of liquid fossil fuels through chemical looping processes - Integration of chemical looping processes in a refinery-

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Abstract

Oil refining processes demand and use vast quantities of energy and thus are responsible for the emission of a great deal of CO₂. In addition, hydrogen is used in oil refineries for hydrodesulfurization and hydrocracking processes. In this sense, the integration of Chemical Looping technology in an oil refinery using vacuum residues as fuel could drive to significant reductions in CO₂ emissions. In this work, Chemical Looping Combustion (CLC) and Chemical Looping Reforming (CLR) experiments have been carried out in a continuously operated 1 kW_{th} unit using a Cu- and Ni-based oxygen carrier, respectively. Diesel, synthetic and mineral lubricant oil were used as fuels as a previous step to the use of low grade residues. Regarding Chemical Looping Combustion conditions, almost 100% of combustion efficiency and full carbon capture were obtained at low oxygen carrier-to-fuel molar ratios ($\phi \geq 1.6$). Regarding Chemical Looping Reforming conditions, a syngas containing a H₂ concentration over 50 vol.% in dry basis was obtained with the additional advantage of reaching 100% CO₂ capture efficiency in the process. In all cases, syngas composition obtained was close to the given by the thermodynamic equilibrium. These results provide a basis for concluding that the integration of Chemical Looping processes for heat/steam and hydrogen production in an oil refinery is feasible and could lead to significant environmental advantages.

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Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: Chemical-Looping Combustion; Chemical-Looping Reforming; Fossil fuels; Refinery; Hydrogen.

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1. Introduction

Chemical Looping technologies stand out for being innovative cost effective solutions for Carbon Dioxide Capture and Storage (CCS) purposes. Chemical Looping processes use a metal oxide as oxygen carrier (OC) in order to avoid direct contact between fuel and air. The OC circulates continuously between two interconnected fluidized beds where it is reduced and oxidized in a cyclic way.

On the one hand, Chemical Looping Combustion (CLC) is one of the most cost-effective design options available for CO₂ capture in power plants as the capture is intrinsic to the combustion process itself. On the other hand, Chemical Looping Reforming (CLR) offers the possibility of integrating CO₂ capture technologies with syngas or H₂ production systems for power generation or fuel applications [1].

CLC and CLR processes are founded on the same principle, with the only difference that the oxygen available under CLR conditions is kept under the stoichiometric values in order to achieve partial combustion of the fuel and therefore obtain a gaseous outlet stream mainly composed by H₂. Due to the different purposes of CLC and CLR, specific OCs must be used in each case. For CLR, Ni based OCs are the most extensively used OCs in this field because of their high selectivity towards H₂ and CO and their ability to enhance the steam reforming reaction [2]. For CLC, a Cu-based OC was selected on account of its cost, which is cheaper than Ni, its high reaction rates, its elevated oxygen transfer capacity and the issue that it has no thermodynamic restrictions to achieve complete fuel conversion to CO₂ and water [1].

During the early stages of investigation, gaseous and solid fuels were the most extensively used but lately there is a growing interest in the application of liquid fossil fuels to Chemical Looping technologies. Recently, several publications have studied the behavior of liquid fossil fuels such as bitumen, dodecane, kerosene and fuel oil [3-8]. Particularly worth noting is the work carried out by Moldenhauer et al. who have published extensively on this issue. They have studied the behavior of synthetic oxygen carriers based on Nickel, Manganese and Copper working with sulfur free kerosene in a continuous 300 Wth CLC unit [5, 6]. Also, they have successfully tested mineral oxygen carriers such as ilmenite with sulfur free kerosene and kerosene containing 0.57 mass% sulfur in the same continuous 300 Wth facility [7] and more recently, they designed and constructed a 10 kWth continuous CLC unit where they were able to work with heavy fuel oil as fuel during long term experiments using ilmenite as oxygen carrier [8].

The integration of chemical looping processes inside an oil refinery could generate important advantages in a CCS context. Since it must be considered that, globally, oil refineries rank third position in stationary CO₂ emissions sources overtaken only by power and cement production facilities and they are responsible for about 4 % of global CO₂ emissions, making a total of approximately 1 billion metric tons of CO₂ per year [9].

CO₂ is emitted at oil refineries facilities from different sources. The major CO₂ emission sources are focused on furnaces and boilers as they account for up to 30-60 % of total CO₂ emissions. The heat required for fuel feeding and to provide the heat necessary to carry out reforming and cracking reactions produce a large amount of CO₂ emissions. Also, it must be taken into consideration that certain amount of H₂ is necessary in oil refineries to be used in several hydro processes: hydrotreating for reducing sulfur, nitrogen and aromatics, and hydrocracking to convert the high-boiling constituent hydrocarbons to more valuable lower-boiling products such as gasoline, kerosene, jet fuel, and diesel oil. In the industry, most refineries produce H₂ in situ by means of steam methane reforming or thanks to a gasifier although in both cases important amounts of CO₂ are generated and emitted into the atmosphere.

In view of the foregoing, it is clear that oil refining processes are energy-intensive and they require considerable amounts of direct or indirect heat and a H₂ source. This situation is particularly troubling also because the environmental quality requirements for oil products are becoming more restrictive. Currently, refineries are dealing with many challenges, the fuel quality demands are increasing, the feeding crude fuel is becoming heavier and the air pollutant emissions are progressively more rigorous [10]. These challenges will severely affect the refinery industry but also will lead to technical innovation. Chemical Looping technologies are proposed as a promising technological alternative for grappling with the issue of CO₂ emissions in refineries.

In this sense, oil refineries produce a large variety of by-products ranging from naphtha to asphalt. Those heavy hydrocarbons may be considered as potential fuels to be used under Chemical Looping conditions to produce heat, steam and H₂ with decreased CO₂ emissions in an integrated way with the refining process.

The main scope of this research was to analyze the employability of several liquid fuels in a continuous Chemical Looping unit under combustion and reforming conditions. Three different liquid fuels were selected: diesel, synthetic/mineral lubricant oil. This represents a previous step to the use of low grade residues obtained in the refinery.

2. Experimental

2.1. Oxygen-carrier

Two OC were used in this work: one was based on CuO and the other on NiO. The first one was used in the CLC process and the second one was used in the CLR process due to it has been demonstrated their good behavior in these processes using other liquid fuel, ethanol, in previous works [11, 12].

Both OC were designated indicating the metal oxide followed by its weight percent in the solid and the support used. CuO14- γ -Al₂O₃ oxygen carrier was prepared by impregnation over commercial γ -Al₂O₃ (Puralox NWa-155, Sasol Germany GmbH) using the criteria given by de Diego et al. [13] to avoid agglomeration problems. The NiO18- α -Al₂O₃ material was prepared by hot incipient wetness impregnation over α -Al₂O₃, which was obtained by calcination of the commercial γ -Al₂O₃ at 1150 °C during 2 hours. The preparation and characterization of these materials could be found more detailed in several works [13, 14]. Table 1 shows the main characteristics of both oxygen-carriers.

Table 1. Physical properties and solid composition of the oxygen carriers.

| | CuO14- γ -Al ₂ O ₃ | NiO18- α -Al ₂ O ₃ |
|--|--|--|
| Density (g cm ⁻³) | 1.50 | 2.40 |
| Oxygen transport capacity, R _{OC} | 0.028 | 0.038 |
| Porosity (%) | 53.7 | 42.5 |
| XRD | γ -Al ₂ O ₃ , CuO, CuAl ₂ O ₄ | α -Al ₂ O ₃ , NiO, NiAl ₂ O ₄ |

2.2. Fossil fuels

Several fossil fuels were used in the evaluation of the CLC and CLR processes: Diesel, synthetic and mineral oil. All fuels are a mix of several hydrocarbons. The Diesel is a mixture of different hydrocarbons between C10 and C20. Synthetic and mineral oil were a mixture of hydrocarbons between C13 and C25. However, the synthetic oil is a combination of different olefins and the mineral oil is a mixture of paraffin's and aromatic compounds. To determine a molecular formula that can represent each fuel it was done the elemental analysis and it was obtained their distillation curve. Fig. 1 shows the distillation curve for the three liquid fuels. According to the composition and based on the 50% volume distilled, the 1-Pentadecyne (C₁₅H₂₈) and the 1-Nonadecene (C₁₉H₃₈) were chosen as representative hydrocarbons for the diesel and the oils, respectively. It has to be keeping in mind that these liquid fuels were used as a previous step for future vacuum residue evaluation as fuel in these chemical looping processes. However, this fuel will probably require a previous desulphurization treatment to avoid their deactivation by sulfur, especially when Ni-based oxygen carriers are used.

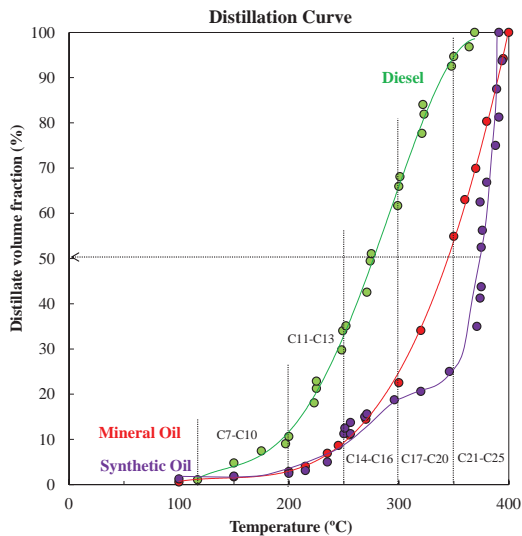


Fig. 1. Distillation curve of the liquid fossil fuels.



Fig. 2. Image of the ICB-CSIC-liq1 prototype.

2.3. Experimental facility, ICB-CSIC-liq1

The experiments were carried out in the pilot plant shown in Fig. 2 and designed by the CSIC group to evaluate the viability of both CLC and CLR processes with different liquid fossil fuels. A detailed explanation of the unit can be found in previous works [11, 12]. The liquid fossil fuel feeding was made by using a peristaltic pump. The fuel was fully evaporated and fed into the FR to react with the oxygen carrier. The reduced OC was transferred to the AR where it was regenerated with air and forced to circulate through the unit.

The gas outlet streams of the FR and AR were drawn to respective on-line gas analyzers to get continuous data of gas composition. The outlet gas from the FR was composed by CO_2 , H_2O , CH_4 , H_2 , and CO . Pure N_2 or depleted air was obtained at the AR outlet. The possible carbon formation on the FR would be detected as CO_2 at the AR outlet. Furthermore, a Gas Chromatograph (Clarus 580 with Model Arnel 4016 PPC and Haye Sep columns) was also established on line to detect the possible hydrocarbon compounds coming from fuel decomposition or reaction.

2.4. Operational Conditions

The main parameter in any chemical looping process is the oxygen-to-fuel molar ratio. To evaluate its effect on the FR gas outlet composition two different methods were used. The first one consisted on controlling the solid circulation rate, in this case between 4 and 8 $\text{kg}\cdot\text{h}^{-1}$. This method was used in the evaluation of the CLC process using the OC based on Cu at FR temperature of 800 °C. The second method was based on controlling the oxygen fed to the AR by diluting the inlet stream with N_2 , varying the oxygen concentration between 2 and 21 vol.%. The latter was used to evaluate the CLR process using the solid based on Ni at FR temperature of 900 °C. An additional advantage of this second method could be the production of pure N_2 at the AR outlet stream.

In all experiments the fuel flow injected into the FR was constant and equal to 0.67 g/min. However, in the CLC experiments the total flow fed to the FR was keep constant at 360 $\text{NI}\cdot\text{h}^{-1}$, and in the CLR experiments it was kept at 150 $\text{NI}\cdot\text{h}^{-1}$ due to the physical differences in the material used.

The steady-state for the different operating conditions was maintained at least for forty minutes in each test which implies that a total of 100 hours of operation was accomplished including CLC and CLR tests.

3. Results and discussion

CO₂, CO, CH₄, and H₂ concentrations and CO₂ and O₂ concentrations at the outlet of the FR and AR streams respectively were measured by on line analyzers. From these measurements, carbon, hydrogen and oxygen mass balances were made to attest that the system was performing as intended for each experiment carried out. The main reactions that take place in the fuel and air reactors are shown in Table 2 for each fuel.

Table 2. Reduction and oxidation reactions in the FR and AR for both Diesel and Mineral oil for any OC based on a metal oxide.

| Diesel | Oil |
|---|--|
| Fuel reactor: | |
| Complete Oxidation | Complete Oxidation |
| $C_{15}H_{28} + 44 MeO \rightarrow 44 Me + 15 CO_2 + 14 H_2O$ (R.1) | $C_{19}H_{38} + 57 MeO \rightarrow 57 Me + 19 CO_2 + 19 H_2O$ (R.15) |
| $CH_4 + 4 MeO \rightarrow 4 Me + CO_2 + 2 H_2O$ (R.2) | $CH_4 + 4 MeO \rightarrow 4 Me + CO_2 + 2 H_2O$ (R.2) |
| $H_2 + MeO \rightarrow Me + H_2O$ (R.3) | $H_2 + MeO \rightarrow Me + H_2O$ (R.3) |
| $CO + MeO \rightarrow Me + CO_2$ (R.4) | $CO + MeO \rightarrow Me + CO_2$ (R.4) |
| Partial oxidation | Partial oxidation |
| $C_{15}H_{28} + 15 MeO \rightarrow 15 Me + 15 CO + 14 H_2$ (R.5) | $C_{19}H_{38} + 19 MeO \rightarrow 19 Me + 19 CO + 19 H_2$ (R.16) |
| Steam reforming catalyzed by Ni | Steam reforming catalyzed by Ni |
| $C_{15}H_{28} + 15 H_2O \rightarrow 15 CO + 29 H_2$ (R.6) | $C_{19}H_{38} + 19 H_2O \rightarrow 19 CO + 38 H_2$ (R.17) |
| $C_{15}H_{28} + 30 H_2O \rightarrow 15 CO_2 + 44 H_2$ (R.7) | $C_{19}H_{38} + 38 H_2O \rightarrow 19 CO_2 + 57 H_2$ (R.18) |
| $CH_4 + H_2O \rightarrow CO + 3 H_2$ (R.8) | $CH_4 + H_2O \rightarrow CO + 3 H_2$ (R.8) |
| Dry reforming catalyzed by Ni | Dry reforming catalyzed by Ni |
| $C_{15}H_{28} + 15 CO_2 \rightarrow 30 CO + 14 H_2$ (R.9) | $C_{19}H_{38} + 19 CO_2 \rightarrow 38 CO + 14 H_2$ (R.19) |
| $CH_4 + CO_2 \rightarrow 2 CO + 2 H_2$ (R.10) | $CH_4 + CO_2 \rightarrow 2 CO + 2 H_2$ (R.20) |
| Carbon chain breakage | Carbon chain breakage |
| $C_{15}H_{28} \leftrightarrow 15 C + 14 H_2 (+CH_4)$ (R.11) | $C_{19}H_{38} \leftrightarrow 19 C + 19 H_2 (+CH_4)$ (R.21) |
| Carbon gasification | Carbon gasification |
| $C + H_2O \rightarrow CO + H_2$ (R.12) | $C + H_2O \rightarrow CO + H_2$ (R.22) |
| $C + CO_2 \rightarrow 2 CO$ (R.13) | $C + CO_2 \rightarrow 2 CO$ (R.23) |
| Water-gas shift | Water-gas shift |
| $CO + H_2O \leftrightarrow CO_2 + H_2$ (R.14) | $CO + H_2O \leftrightarrow CO_2 + H_2$ (R.24) |
| Air Reactor: | |
| $Me + \frac{1}{2} O_2 (air) \rightarrow MeO (+ N_2)$ (R.25) | |
| Carbon combustion | |
| $C + O_2 \rightarrow CO_2$ (R.26) | |

3.1. Chemical looping combustion process

The oxygen carrier-to-fuel ratio, ϕ , which is defined as the ratio between the oxygen supplied by the oxygen carrier and the oxygen needed for stoichiometric combustion of the fuel, was calculated by Eq. (1) as follows:

$$\phi = \frac{F_{OC}}{b \cdot F_{Fuel}} \quad (1)$$

where F_{OC} is the molar flow rate of the OC, which is calculated considering both the solid flow rate (measured by means of a diverting solids valve located below the cyclone, see Fig. 2) and the metal oxide content of the OC. F_{Fuel} is the inlet molar flow rate of the fuel into the FR. b is the stoichiometric value of the complete oxidation reaction, which is equal to 44 and to 57 for diesel and oil, respectively (R.1 and R.15). A value of $\phi = 1$ corresponds to the stoichiometric MeO amount needed for complete conversion of the fuel to CO_2 and H_2O .

One way to evaluate the chemical looping process is through the combustion efficiency (η_c), which is related with the CO_2 production, and defined as the ratio between the oxygen given by the oxygen carrier in the FR outlet gas and the stoichiometric oxygen needed for complete fuel combustion, Eq (2).

$$\eta_c = \frac{(2x_{CO_2} + x_{CO} + x_{H_2O})_{out} \cdot F_{out} - x_{Fuel} \cdot F_{in}}{(b \cdot x_{Fuel})_{in} \cdot F_{in}} \cdot 100 \quad (2)$$

where F_{in} and F_{out} are the inlet and outlet molar gas flow rates and x_i is the gas molar fraction of component i . The fuel combustion is complete to CO_2 and H_2O when η_c reaches the value of 100.

Fig. 3 and 4 show the combustion efficiency, η_c , as a function of ϕ for the liquid fuels tested. Combustion efficiencies higher than 90% were obtained in all cases and full combustion was obtained at low oxygen carrier-to-fuel molar ratios. This is a consequence of the high reactivity of the oxygen carrier employed.

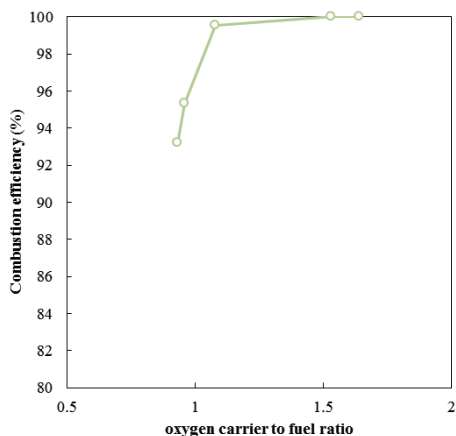


Fig. 3. Effect of the oxygen carrier-to-Diesel molar ratio on combustion efficiency. $T = 800$ °C.

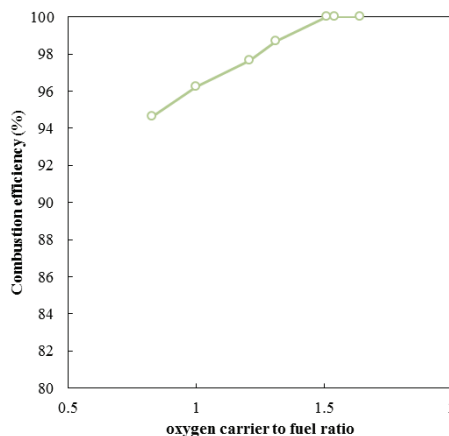


Fig. 4. Effect of the oxygen carrier-to-oil molar ratio on combustion efficiency. $T = 800$ °C.

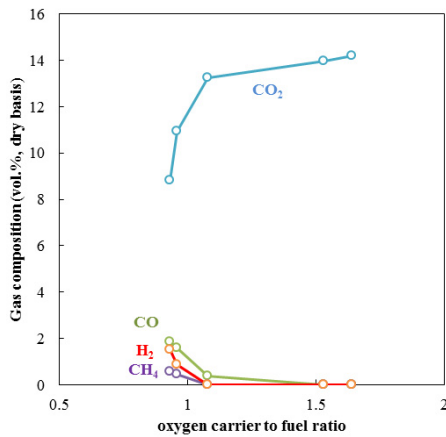


Fig. 5. Gas product distribution at the outlet of the FR using diesel as fuel. T = 800 °C.

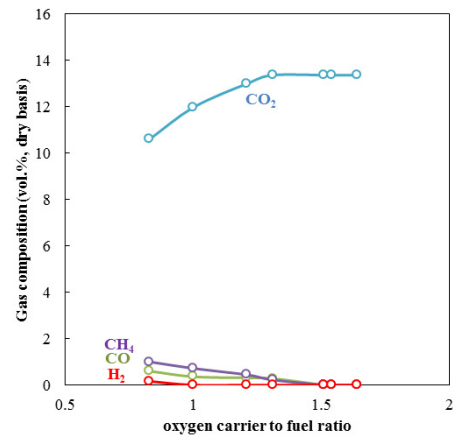


Fig. 6. Gas product distribution at the outlet of the FR using synthetic oil as fuel. T = 800 °C.

To deeply analyze the combustion efficiency obtained, Fig. 5 and 6 shows the gas product distribution obtained during the combustion tests. CH₄, CO and H₂ were the main unburnt products obtained at the FR outlet. No other hydrocarbons but CH₄ were detected in any of the experiments tested. It was also reached a full conversion of both fuels, based on mass balances done to the system.

3.2. Chemical looping reforming process

For the CLR process the control of the oxygen fed into the FR transported by the oxygen carrier for syngas production was made by controlling the amount of oxygen fed to the AR. In this case, the oxygen carrier-to-fuel molar ratio parameter is redefined as the O_{NiO}/Fuel molar ratio, which is mol of oxygen transferred by the OC from the AR to the FR per mol of fuel injected to the FR.

In any CLR process, the O_{NiO}/Fuel molar ratio is considered as the main parameter [12, 15]. For instance, in the case of diesel an O_{NiO}/Fuel molar ratio equal or higher than 44 implies that the reaction that takes place in the FR is the complete reaction (R.1). If $15 < O_{NiO}/diesel < 44$ the contribution of the complete reaction decreases and the partial oxidation and reforming reactions (R.5 and R.6-R.8) show up, increasing the syngas production. If the O_{NiO}/diesel molar ratio took values lower than 15 there was not enough oxygen and carbon formation reaction would take place (R.11). This carbon obtained could be gasified in presence of water or CO₂ inside the FR (R.12 and R.13). The water gas shift (WGS) reaction must be considered (R.14). The theoretical behavior of the mineral oil is the similar as diesel based on the reactions: Complete reaction (R.15), partial oxidation reaction (R.16), reforming reactions (R.17-R.18) and the carbon formation reaction (R.21).

Fig. 7 and 8 show the syngas obtained as a function of the O_{NiO}/Fuel molar ratio using both diesel and mineral oil as fuel. These results correspond to data without water addition. In addition, data corresponding to the thermodynamic equilibrium obtained with the HSC Chemistry 6.1 software [16] were represented by the continuous lines. It can be seen that for any value of O_{NiO}/fuel molar ratio above the given by the complete oxidation reactions (R.1 and R.15) the gas composition produced is almost CO₂ and H₂O. If this value decreases, the H₂ and CO concentration increases due to the major contribution of the rest of the reactions. If the molar ratio takes values lower than the one given by the partial oxidation (R.5 and R.16), carbon is formed. This implies a decrease of the CO₂ capture efficiency as a consequence of the CO₂ produced by the carbon combustion in the AR (R.26). It is also remarkable that all experimental data were very close to the thermodynamic equilibrium.

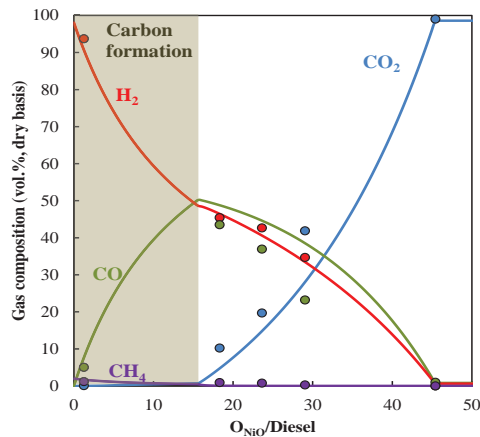


Fig. 7. Gas product distribution as a function of $O_{NiO}/diesel$ molar ratio. Continuous lines=thermodynamic equilibrium.

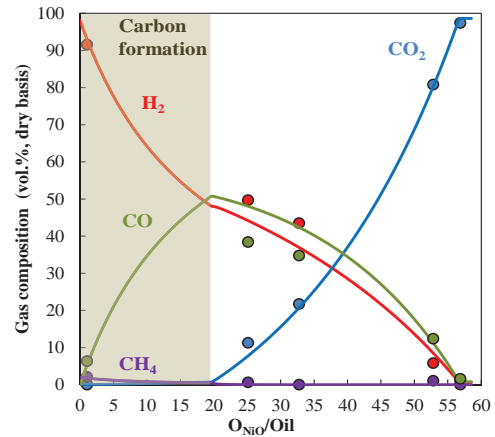


Fig. 8. Gas product distribution as a function of O_{NiO}/oil molar ratio. Continuous lines=thermodynamic equilibrium.

4. Conclusions

Combustion and reforming of fossil fuels in Chemical-looping processes (CLC and CLR) have been investigated in a 1 kW_{th} unit using two oxygen carriers based on Cu and Ni, respectively. The effect of the oxygen carrier-to-fuel molar ratio on the FR outlet gas product composition was analyzed for different liquid fossil fuels.

It was found that a complete conversion of each fossil fuel evaluated was achieved at all operating conditions. Neither diesel nor any oil were detected at the outlet of the FR.

Regarding the CLC process, the most important parameter affecting to the gas composition was the oxygen carrier-to-fuel molar ratio, ϕ . Complete conversion of each fuel to CO₂ and H₂O was reached at ϕ values higher than 1.6, which leads to 100% of carbon capture in the process.

For the CLR process the oxygen transferred from the AR to the FR was controlled by the oxygen supplied to the AR. It was observed that this control method allows an accurate oxygen flow from the AR to the FR, and, in addition, pure N₂ is obtained at the outlet of the AR. In this work, a syngas containing a H₂ concentration over 50 vol.% in dry basis was obtained with the additional advantage of reaching 100% CO₂ capture efficiency in the process. It was also determined that the experimental results were close to the data given by the theoretical equilibrium.

Based on the tests carried out, it was concluded that these oxygen carriers could be suitable for CLC and CLR processes, working with liquid fossil fuels.

These results allowed concluding that Chemical Looping processes could be integrated in an oil refinery process leading to significant reductions in CO₂ emissions.

CLC technology can be incorporated to furnaces and boilers for the production of heat and steam meanwhile hydrogen production by means of a CLR process can be integrated in a refinery for hydrotreating and hydrocracking processes.

Acknowledgements

This work was partially supported by the Spanish Ministry for Science and Innovation (MICINN, project ENE2011-26354, ENE2014-56857-R), European Regional Development Fund (ERDF) and by the Government of Aragón (Spain, DGA ref. T06). A. Serrano also thanks the Spanish Ministry of Economy and Competitiveness for the F.P.I. fellowship.

References

- [1] Adánez J, Abad A, García-Labiano F, Gayán P, de Diego LF. Progress in chemical-looping combustion and reforming technologies. *Prog Energy Combust Sci* 2012; 38: 215-82.
- [2] Zafar Q, Mattisson T, Gevert B. Redox investigation of some oxides of transition-state metals Ni, Cu, Fe, and Mn supported on SiO₂ and MgAl₂O₄. *Energy Fuel* 2006; 20: 34-44.
- [3] Hoteit A, Forret W, Pelletant W, Roesler J, Gauthier T. Chemical Looping Combustion with different types of liquid fuels. *Oil & Gas Science and Technol* 2011; 66: 193-99.
- [4] Cao Y, Li B, Zhao HY, Lin CW, Sit SP, Pan WP. Investigation of asphalt (bitumen)-fuelled Chemical Looping Combustion using durable copper-based oxygen carrier. *Energy Procedia* 2011; 4: 457-64.
- [5] Moldenhauer P, Rydén M, Mattisson T, Lyngfelt A. Chemical-looping combustion and chemical-looping reforming of kerosene in a circulating fluidized-bed 300W laboratory reactor. *Int J Greenhouse Gas Control* 2012; 9: 1-9.
- [6] Moldenhauer P, Rydén M, Mattisson T, Lyngfelt A. Chemical-looping combustion and chemical-looping with oxygen uncoupling of kerosene with Mn- and Cu- based oxygen carriers in a circulating fluidized-bed 300W laboratory reactor. *Fuel Process Technol* 2012; 104: 378-89.
- [7] Moldenhauer P, Rydén M, Mattisson T, Younes M, Lyngfelt A. The use of ilmenite as oxygen carrier with kerosene in a 300W CLC laboratory reactor with continuous circulation. *Appl Energy* 2014; 113: 1846-54.
- [8] Moldenhauer P, Rydén M, Mattisson T, Hoteit A, Jamal A, Lyngfelt A. Chemical-Looping Combustion with Fuel Oil in a 10 kWth Pilot Plant. *Energy Fuels* 2014; 28: 5978-87.
- [9] Gale J. Sources of CO₂ Carbon Dioxide Capture and Storage. In: Metz B, Davidson O, de Coninck H, Loos M, Meyer L, editors. *Special Report on Carbon Dioxide Capture and Storage*. Intergovernmental Panel on Climate Change. New York: Cambridge University Press; 2005. p. 75-104.
- [10] Swaty T. Global refining industry trends: the present and future. *Hydrocarbon Processing* 2005; 84: 35-46.
- [11] de Diego LF, Serrano A, García-Labiano F, García-Díez E, Abad A, Gayán P, Adánez J. Bioethanol combustion with CO₂ capture in a 1 kW_{th} Chemical Looping Combustion prototype: Suitability of the oxygen carrier. *Chem Eng J* 2016; 283: 1405-13.
- [12] García-Labiano F, García-Díez E, de Diego LF, Serrano A, Abad A, Gayán P, Adánez J, Ruíz JAC. Syngas/H₂ production from bioethanol in a continuous chemical-looping reforming prototype. *Fuel Process Technol* 2015; 137: 24-30.
- [13] de Diego LF, Gayán P, García-Labiano F, Celaya J, Abad A, Adánez J. Impregnated CuO/Al₂O₃ oxygen carrier for Chemical-looping combustion: avoiding fluidized bed agglomeration. *Energy Fuels* 2005; 19: 1850-56.
- [14] Gayán P, Dueso C, Abad A, Adánez J, de Diego LF, García-Labiano F. NiO/Al₂O₃ oxygen carriers for Chemical-looping combustion prepared by impregnation and deposition-precipitation methods. *Fuel* 2009; 88: 1016-23.
- [15] García-Díez E, García-Labiano F, de Diego LF, Abad A, Gayán P, Adánez J, Ruíz JAC. Optimization of hydrogen production with CO₂ capture by autothermal Chemical-looping Reforming using different bioethanol purities. *Applied Energy* 2016; 169: 491-98.
- [16] HSC Chemistry 6.1. Chemical reaction and equilibrium software with thermochemical database and simulation module. Pori, Finland: Outotec Res Oy 2008.