

# Chemical Looping Combustion Process applied to liquid fuels

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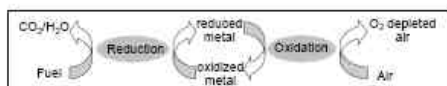
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## Abstract

Chemical looping combustion (CLC) process is an oxy-combustion technology in which the oxygen required for combustion is supplied by metal oxides known as oxygen carriers. The objective of the present work is to investigate the feasibility of liquid feed injection and contact with oxygen carrier under CLC conditions.  $\text{NiAl}_{0.44}\text{O}_{1.67}$  was used as oxygen carriers in a fluidized bed reactor and dodecane as the combustible. The batch fluidized bed experiment results showed that during the reduction period, all the dodecane was converted. A high concentration of  $\text{CO}_2$  (> 99%) could be achieved. There is no formation of carbon on the oxygen carrier during the reduction step. In this study, the combustion of dodecane was carried out successfully, producing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  at 100% fuel conversion with stable operation.

## Introduction

Chemical looping combustion (CLC) is a flameless combustion technology where there is no direct contact between air and fuel. Theoretical analyses of the technology indicate that its use results in increased power efficiency compared to regular combustion [1]. The important feature in the chemical looping combustion is that the carbon dioxide produced from the reduction step is inherently separated from the inert nitrogen and unreacted oxygen from the combustion air. Carbon dioxide is easily separated from the water by condensation of the water. This makes pure carbon dioxide available for sequestration. The combustion process does not produce  $\text{NO}_x$ . The production of a sequestration ready  $\text{CO}_2$  stream does not require any additional separation units and there is no energy penalty or reduction in power plant efficiency. This combustion process is divided into two steps (see Figure 1) : reduction and oxidation.



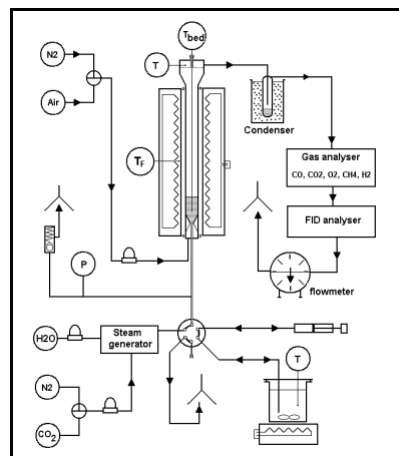
**Figure 1: Principle of chemical looping combustion**

The majority of the work performed to date on CLC has been performed using methane and coal as the fuel. There are numerous literature investigations pertaining to CLC with gaseous [2,3] and solid fuels [4,5]. There are only limited studies with oxygen carriers used to combust liquid fuels. The application of chemical looping for heat production from liquid fuels such as heavy hydrocarbons is gaining wide interest in the oil and refining industry. The use of liquid fuels raises specific problems of implementation that are different than for gas or solids.

An experimental study was performed to identify the ability of  $\text{NiAl}_{0.44}\text{O}_{1.67}$  to convert liquid fuel to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Experiments have been performed in a fluidized bed unit operating in batch mode, using dodecane as a fuel.

## Experimental set-up

The scheme hereafter (see Figure 2) presents the experimental pilot scale. It consists of a fluidized bed reactor made of quartz with 20-mm inner diameter. The reactor was electrically heated up to  $950^\circ\text{C}$  and was operated at atmospheric pressure. 45g of oxygen carrier were preheated in an inert atmosphere ( $\text{N}_2$ ) to the desired experimental temperature and then exposed to air to ensure that the particles were fully oxidized before the reduction period.



**Figure 2: Experimental setup**

During reduction steps, the liquid fuel is punctually injected at the bottom of the dense bed. The combustion gas sample was pumped to a water condenser. The  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{HC}$  and  $\text{CH}_4$  gas

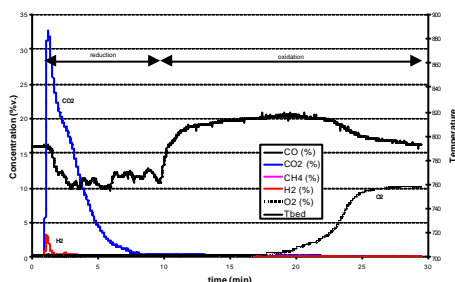
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concentrations were then measured. Data are recorded using a data acquisition system connected to a personal computer running TestPoint software. The acquisition frequency is 1 Hz

#### Dodecane injection on $\text{NiAl}_{0.44}\text{O}_{1.67}$

The oxygen present in 45g of nickel based oxygen carrier ( $\text{NiAl}_{0.44}\text{O}_{1.67}$ ) totally oxidized is 12.3g. This amount is in excess regarding the amount of oxygen needed to fully convert 1 mL of dodecane (2.6g) into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

After introduction of dodecane into the reactor,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were formed and no  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$  were observed during the carrier reduction time, thus indicating that dodecane conversion was complete (see Figure 3). This figure shows also a decrease of the bed temperature due to the endothermic reduction of metal oxide. Upon  $\text{O}_2$  introduction to the reactor,  $\text{CO}$  and  $\text{CO}_2$  was not detected at the reactor outlet stream. This result indicate that there was no carbon formed in the reduction step. It must be noted that the slight peak of hydrogen measured during the increase of  $\text{CO}_2$  concentration ( $1 < t < 1.5$  min) is an artifact: it comes from internal compensation calculation of interference of  $\text{CO}_2$  on hydrogen by the analyzer.

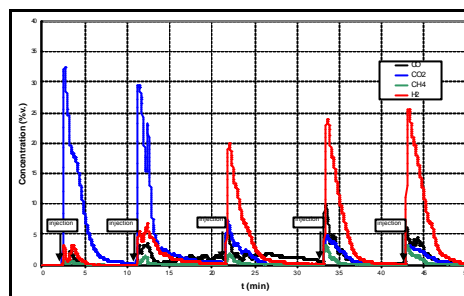


**Figure 3: Outlet gas concentration after the injection of dodecane on  $\text{NiAl}_{0.44}\text{O}_{1.67}$  at  $800^\circ\text{C}$**

Figure 4 shows flue gas concentration for five consecutive injections of dodecane on a bed of 45g of  $\text{NiAl}_{0.44}\text{O}_{1.67}$  at  $800^\circ\text{C}$ . Five injections of 1 mL of dodecane are performed at  $t = 2.0$ ; 10.7; 21.1; 32.7 et 42.6 min, without intermediate oxidation.

We observe that for the two first injections of dodecane, the conversion of dodecane is complete. This result indicates that, during the second injection time, the amount of available oxygen stored in the oxygen carrier is still sufficient to convert dodecane into  $\text{CO}_2$  and steam.

Figure 4 shows also the selectivities to synthesis gas. During the third injection,  $\text{CO}$  and  $\text{H}_2$  and  $\text{CH}_4$  was detected at the reactor outlet stream. The shift in the reaction is due to the quantity of  $\text{O}_2$  present in the oxygen carrier at the moment of dodecane injection.



**Figure 4: Outlet gas concentration for five consecutive injections of 1 mL of dodecane on  $\text{NiAl}_{0.44}\text{O}_{1.67}$  at  $800^\circ\text{C}$  Conclusions**

Experiments presented in this paper extend the feasibility of the Chemical Looping Combustion (CLC) process to liquid fuels. It was shown that dodecane is totally converted into  $\text{CO}_2$  and steam using  $\text{NiAl}_{0.44}\text{O}_{1.67}$  oxygen carrier. No carbon deposits was detected during the reduction step, resulting in an optimal  $\text{CO}_2$  capture efficiency. The CLC process can therefore be used to produce energy with a pure flow of  $\text{CO}_2$  which than can be easily sequestered. Chemical looping reforming could be useful for production of synthesis gas or for cogeneration of  $\text{H}_2$  and power.

#### Acknowledgements

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