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

F. García-Labiano*, L.F. de Diego, E. García-Díez, A. Serrano, A. Abad, P. Gayán, J. Adánez

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza, Spain

Abstract

Oil refining processes demand and use vast quantities of energy and thus are responsible for the emission of a great deal of CO_2. In addition, hydrogen is used in oil refineries for hydrodesulfurization and hydrocraking 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 CO_2 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 ($\phi \geqslant 1.6$). Regarding Chemical Looping Reforming conditions, a syngas containing a H_2 concentration over 50 vol.% in dry basis was obtained with the additional advantage of reaching 100% CO_2 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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Keywords: Chemical-Looping Combustion; Chemical-Looping Reforming; Fossil fuels; Refinery; Hydrogen.

* Corresponding author. Tel.: +34-976-733977; fax: +34-976-733318.
E-mail address: glabiano@icb.csic.es

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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 CO_2 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 CO_2 capture technologies with syngas or H_2 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 H_2. 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 H_2 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 CO_2 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 us 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 CO_2 emissions sources overtaken only by power and cement production facilities and they are responsible for about 4 % of global CO_2 emissions, making a total of approximately 1 billion metric tons of CO_2 per year [9].

CO_2 is emitted at oil refineries facilities from different sources. The major CO_2 emission sources are focused on furnaces and boilers as they account for up to 30-60 % of total CO_2 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 CO_2 emissions. Also, it must be taken into consideration that certain amount of H_2 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 H_2 in situ by means of steam methane reforming or thanks to a gasifier although in both cases important amounts of CO_2 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 H_2 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 CO_2 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 H_2 with decreased CO_2 emissions in an integrated way with the refining process.