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Steam, dry, and steam-dry chemical looping reforming of diesel fuel in a 1 kW_{th} unit

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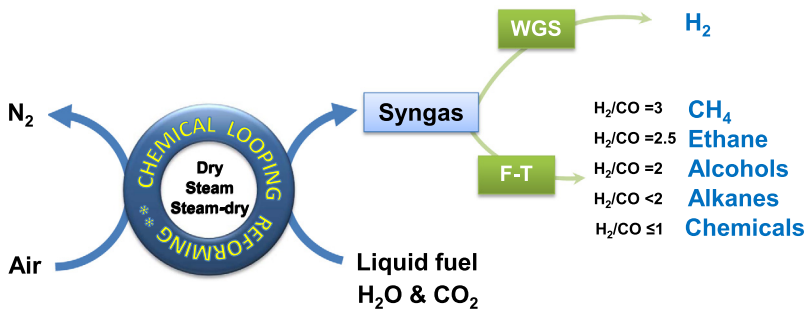
HIGHLIGHTS

- Syngas production using autothermal chemical looping reforming (CLR) of liquid fossil fuels.
- Steam, dry and steam-dry reforming is accomplished.
- >20 h of continuous operation in a 1 kW_{th} CLR unit.
- Any H_2/CO molar ratio between 0.2 and 3 achieved for H_2 production or Fischer-Tropsch reactions.
- Pure N_2 is obtained in the AR, useful for NH_3 production.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemical looping reforming (CLR) is a process that enables the production of syngas/H_2 with CO_2 capture by using oxygen carriers that prevent direct contact between the fuel and air. This work presents the experimental results obtained in a 1 kW_{th} CLR unit using a Ni-based oxygen carrier and diesel as fuel, as a first trial for further advancement with heavier liquid fuels. The influence of the main operating conditions, such as oxygen-to-diesel molar ratio and the H_2O and/or CO_2 feed into the system, was analysed in both steam and dry CLR processes. In addition, the combined steam-dry CLR process enabled the production of syngas with any H_2/CO molar ratio between 0.2 and 3, which resulted in a wide variety of final products during its use in Fischer-Tropsch processes. In all cases, the syngas composition was close to that given by the thermodynamic equilibrium. These results demonstrate the technical feasibility of steam, dry, and combined steam-dry reforming processes for liquid fossil fuels in a chemical looping system.

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1. Introduction

The CO_2 concentration in the atmosphere is continuously increasing, with values above 400 ppm reached last year [1]. For this reason, new energetic processes and resources with a low carbon footprint have gained increasing relevance in recent years. Although there is growing interest in renewable sources, estimates show that petroleum will be still the main primary energy source until 2040, responsible for 36% of production, followed by natural gas at 30% [2]. However, given the importance of petroleum to the worldwide economy and its associated environmental impact, it would be necessary to implement carbon capture and storage (CCS) technologies to reduce greenhouse gas emissions in the refining processes [3]. Of the available CCS technologies, chemical looping (CL) processes are considered to be promising owing to their reduced cost [4].

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Chemical looping reforming (CLR) is a process for the production of syngas with CO_2 capture [5]. The CLR system is based on the partial oxidation and subsequent reforming of the fuel, to produce syngas ($CO + H_2$) while preventing direct contact between air and fuel through the use of a solid oxygen carrier. This oxygen carrier circulates between two interconnected fluidized-bed reactors. The oxygen carrier reacts with the fuel in the fuel reactor (FR), giving rise to the partial oxidation and reforming of the fuel. Ni-based oxygen carriers are the most common materials used in CLR due to the catalytic activity of metallic Ni in reforming reactions [6,7]. Although other, more environmental friendly and cheaper metal oxides have been considered in chemical looping processes to replace nickel oxide, this material is still preferred for those processes that include reforming reactions. The reduced oxygen carrier reacts with air in the air reactor (AR) and is regenerated. A major advantage of this process is the possibility to obtain pure N_2 at the AR outlet stream by controlling the air entering the AR [8]. Another advantage of the CLR process is that the heat needed for the endothermic reforming reactions taking place in the FR is provided by the hot solid transported from the AR to the FR. Hence, the CLR process does not need any external heat source [9]. In fact, previous works have demonstrated the possibility of operating at autothermal conditions using methane or bioethanol [9,10].

The CLR process with gaseous fuels has been evaluated under different operating conditions at atmospheric pressure in continuous units, at scales ranging from 300 W to 140 kW_{th} [5,6,11–13]. Different liquid fuels, such as sulphur-free kerosene [14] and bioethanol [15], have recently been used with good results.

The syngas obtained in the CLR process can be used for several purposes. The first is H_2 production, which can be achieved by integrating a CLR system, a water gas shift (WGS) reactor, an absorption process, and a pressure swing adsorption (PSA) unit, as seen in Fig. 1a. In this process, H_2O is used as the reforming agent for H_2 production, i.e. by means of a steam CLR process. Half of the hydrogen produced worldwide is used for ammonia production [16], and a quarter is used for hydrotreating and hydrocracking in refineries [16–18]. The CLR process presents a significant advantage for the NH_3 production industry, since it is possible to obtain syngas/H_2 and pure N_2 simultaneously under autothermal conditions [8].

Another interesting option would be the use of syngas for Fischer-Tropsch processes [19–22]. It should be considered, however, that these processes usually operate at high pressure, 20–30 bars. An experimental evaluation of the pressurised CLR process using CH_4 as a fuel was carried out by Ortiz et al. [23] in a semi-continuous fluidized bed. They found similar syngas compositions at both atmospheric and pressurised conditions. However, the pressurised operation of CLR processes including fluidized beds is far from becoming a reality in a near future. Therefore, a syngas compression step should be included in between.

In a Fischer-Tropsch process, different H_2/CO molar ratios are needed depending on the desired final product, i.e. a $H_2/CO = 3$ for methanol production, 2.5 for ethanol, ≤ 2 for general processes including production of alkanes/alcohols, =1 for oxo synthesis, and <1 for synthesis of long chain hydrocarbons producing CO_2 as a by-product [20–22]. To reach this range of syngas composition, a feed of reforming agents (water and/or CO_2) should be necessary. Fig. 1b and c show the scheme of dry CLR and steam-dry CLR units, respectively, for the further use of syngas in Fischer-Tropsch processes. The dry reforming process has been evaluated in the past using gaseous fuels. Dry reforming of methane allows H_2/CO molar ratios to be lowered with the advantage of reducing the carbon footprint [24]. Khani et al. [25] reported the possibility of obtaining different H_2/CO molar ratios by using a combination of dry-steam reforming with methane as fuel. However, no research on dry reforming or steam-dry reforming processes using liquid fuels has been found in the literature.

The aim of this work was to determine the existence of any evidence that would prevent the technical feasibility of syngas production using liquid fossil fuels. Diesel oil was selected as a representative liquid fuel for further evaluations of other heavier liquid hydrocarbons. The effect of the main operational conditions on the syngas production composition, i.e. H_2/CO molar ratio, was evaluated in a 1 kW_{th} CLR unit for steam, dry, and combined steam-dry CLR processes. The novelty of the work is therefore twofold: the first-time use of diesel as feedstock in a CLR process, and the possibility of performing combined dry-steam CLR to vary syngas composition.

2. Experimental

2.1. Materials

2.1.1. Fossil fuel

Commercial diesel oil was used as the fuel in the CLR process. Diesel is comprised of 86.3 wt% carbon and 13.7 wt% hydrogen, with a negligible presence of sulphur and nitrogen. In addition, the distillation curve of the diesel was determined by using a standard method (ISO 3405:2011) [26], see Fig. 2. The 5% and 95% distilled volume fractions of diesel are produced at temperatures of 162 °C and 354 °C, respectively. This would correspond to a mixture of different paraffins and aromatic compounds between C_7 and C_{20}. An empirical molecular formula corresponding approximately to the 50 vol% distilled fraction was assumed for the diesel: $C_{15}H_{28}$. This formula was used to calculate the equilibrium data in the CLR process.

2.1.2. Oxygen carrier

A Ni-based oxygen carrier, NiO18-αAl_2O_3, was used in this work. This oxygen carrier, containing 18 wt% of NiO, has been patented by CSIC [27]. It was obtained by the hot incipient wet impregnation method using α-Al_2O_3 as support, which was obtained by calcination of commercial γ-Al_2O_3 (Puralox NWa-155, Sasol Germany GmbH). The physical characteristics of the oxygen carrier and the inert support were presented in previous works [15,28]. Specifically, the size of the solid was 100–300 μm; the apparent density of the oxygen carrier was 2500 kg/m^3; and the oxygen transport capacity (R_{oc}) was 3.8%. X ray diffraction (XRD) analysis showed the presence of two different compounds, NiO and $NiAl_2O_4$. Although they exhibit different reactivities, both compounds are active for oxygen transference [29]. The catalytic activity and the oxidation and reduction kinetics of the oxygen carrier were also determined in previous works [28,30]. The sintering temperature of this type of Ni-based material is very high, with values of about 1800–2000 °C for the different compounds existing inside the oxygen carrier (Ni, NiO, $NiAl_2O_4$, Al_2O_3). Therefore, the reactivity of the oxygen carrier is more affected by the structural changes undergone by the material during successive redox reactions than by the operating temperature.

2.2. Experimental facility

A 1 kW_{th} CLR prototype, which was designated as ICB-CSIC-liq1, was used. The schematic diagram of the prototype is shown in Fig. 3, and a detailed description of the unit can be found elsewhere [15]. In this work, diesel oil and water were injected into a heater (8) by means of two peristaltic pumps (10). Once evaporated, the liquids were fed into the FR (1) together with N_2 as an inert carrier gas. The temperature in the heater was kept constant at 450 °C, to ensure that the injected liquid fuels were completely evaporated.

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