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Hydrogen production by chemical-looping reforming in a circulating fluidized bed reactor using Ni-based oxygen carriers

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ABSTRACT

This work presents the experimental results obtained during auto-thermal chemical-looping reforming (CLR) in a 900 W_{th} circulating fluidized bed reactor under continuous operation using methane as fuel. Two oxygen carriers based on NiO and supported on γ-Al_2O_3 and α-Al_2O_3 were used during more than 50 h of operation with each oxygen carrier. During operation the effect of different operating variables, like fuel reactor temperature, H_2O/CH_4 molar ratio and solid circulation rate, on CH_4 conversion and gas product distribution was analyzed. It was found that in all operating conditions CH_4 conversion was very high (>98%) and the most important variable affecting to the gas product distribution was the solid circulation rate, that is, NiO/CH_4 molar ratio. Similar gas product distribution was obtained working with both oxygen carriers although at different NiO/CH_4 molar ratios. The oxygen carrier of NiO on α-Al_2O_3 needed lower NiO/CH_4 molar ratio to reach the same gas product composition than the oxygen carrier of NiO on γ-Al_2O_3. Working at optimal operating conditions, 2.5 moles of H_2 per mol of CH_4 could be obtained in this process.

During operation the oxygen carrier particles maintained their physical and chemical properties. These results suggest that these oxygen carriers could have a high durability, being suitable oxygen carriers for a CLR system.

1. Introduction

It is widely accepted today that carbon dioxide coming from fossil fuel combustion is the most important greenhouse gas contributing to global warming. One of the options to overcome anthropogenic greenhouse effect is the development of CO_2 capture and storage technologies from flue gases of power plants. However, CO_2 capture technology applied to transport sector is more complex, being the use of H_2 as fuel one possible option to reduce the CO_2 emissions.

Steam reforming of CH_4 is the most widely used technology for H_2 production, although, this method produces also large amounts of CO_2 as by-product. CO_2 capture technology integrated with H_2 production is available today being high cost the main barrier to its use. In the CACHET project the integration of CO_2 capture technologies with H_2 production systems for power generation and fuel applications are being studied [1]. The overall goal of the CACHET project is to develop innovative technologies which will substantially reduce the cost of CO_2 capture whilst simultaneously producing H_2 from natural gas fuel. Some of the technologies investigated are based in chemical-looping combustion (CLC) process.

CLC is a novel combustion technology with inherent separation of the greenhouse gas CO_2 that involves the use of an oxygen carrier, which transfers oxygen from air to the fuel avoiding the direct contact between them. CLC system is made of two interconnected reactors, designated as air and fuel reactors. In the fuel reactor, the fuel gas (C_nH_{2m}) is oxidized to CO_2 and H_2O by a metal oxide (MeO) that is reduced to a metal (Me) or a reduced form of MeO. The metal or reduced oxide is further transferred into the air reactor where it is oxidized with air, and the material regenerated is ready to start a new cycle. The flue gas leaving the air reactor contains N_2 and unreacted O_2. The exit gas from the fuel reactor contains only CO_2 and H_2O. After water condensation, almost pure CO_2 can be obtained with little energy lost for component separation.

Chemical-looping reforming (CLR) also uses the metal oxide to transfer oxygen to the fuel, being the main difference that the desired product is syngas (H_2 + CO). In the CLR process the air to fuel ratio is kept low to prevent the complete oxidation of the fuel to CO_2 and H_2O. The major advantage of this process is that the heat needed for converting CH_4 to H_2 is supplied without costly oxygen production, without mixing of air with carbon containing fuel gases or without using part of the H_2 produced in the process. An important aspect to be considered in an auto-thermal CLR system is the heat balance. The oxidation reaction of the metal oxide is very exothermic, however, the reduction reactions are endothermic. So, the heat for the endothermic reduction reactions is given

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