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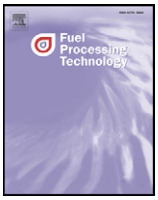

Research article

Chemical looping reforming in packed-bed reactors: Modelling, experimental validation and large-scale reactor design

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ABSTRACT

This paper addresses the experimental demonstration and model validation of chemical looping reforming in dynamically operated packed-bed reactors for the production of H_2 or CH_3OH with integrated CO_2 capture. This process is a combination of auto-thermal and steam methane reforming and is carried out at high pressure, as typical for reforming processes, and at relatively low to intermediate temperatures (ranging from 600 to 900 °C). The oxidation of the oxygen carrier is performed with air and the hot depleted air stream is fed to a gas turbine, which contributes to reduce the electricity demand. After oxidation, a low-grade fuel is used for the reduction of the oxygen carrier, e.g. off-gas from a PSA unit or non-condensable species from methanol synthesis and, when the bed is completely reduced, natural gas diluted with H_2O and CO_2 is reformed while the reactor is cooled down.

An experimental campaign has been carried out in a 2 kW_{th} packed-bed reactor using 500 g of NiO supported on $CaAl_2O_4$ as reforming catalyst and oxygen carrier. This material has demonstrated very high stability over >400 h of consecutive redox and reforming cycles. Due to the flexibility of the process, dry, wet and steam reforming compositions have been tested during the reforming phase. A 1D reactor model has been validated with the obtained experimental results, including also a detailed thermal model to account for the inevitable heat losses of the system. The experimental and model results are in good agreement in terms of breakthrough curves and temperature profiles. The experimental campaign during reforming also confirmed the possibility to carry out the heat removal phase by means of endothermic methane reforming.

The validated reactor model has subsequently been used for the simulation of different configurations in terms of heat management in which the different phases (oxidation, reduction and reforming) are simulated in series. In these analyses, the reactor design and performance have been compared for two plant configurations based on H_2 and CH_3OH production integrated with CO_2 capture. For the case of H_2 production, the CH_4 conversion is 92% and all the CO_2 is captured from the plant, while for CH_3OH production the CH_4 conversion reaches 90% and all carbon species, except CH_3OH, are converted into CO_2, which is separated with high purity.

1. Introduction

Steam reforming is the established process for H_2 production [1] and for syngas production for the manufacture of methanol [2]. Natural gas reforming is carried out in multi-tubular fixed bed reactors using an external furnace to provide the heat of reaction (FTR) or in an auto-thermal reforming (ATR) system using an oxidant (i.e. air or pure oxygen) [1,3–5]. Based on the current process, the following equilibrium limited reactions of steam methane reforming (SMR (1)), and water gas shift (WGS (2)) are identified:

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \qquad \Delta H_0^{298K} = 206.2 kJ/mol \tag{1}$$

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad \Delta H_0^{298K} = -41.2 kJ/mol \tag{2}$$

Conventional steam reforming processes are based on several conversion and separation steps, which include feedstock pre-treatment and removal of sulfur compounds (the catalyst used in steam reforming is extremely sensitive to sulfur and therefore the concentration is kept below 0.5 ppm), high temperature reforming, water gas shift reactor(s) and a final pressure swing adsorption (PSA) unit in order to reach a H_2 purity in the order of 99.999%. The conventional plants lead to high CO_2

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emissions (about 0.8 kg_{CO2}/Nm^3H_2) to the atmosphere, because the PSA-off-gas and part of the input natural gas are burnt in the furnace to supply the heat for the endothermic reforming reaction. In order to reduce CO_2 emissions, CO_2 can be separated from the H_2-rich syngas downstream of the WGS reactor using an MDEA scrubber [6,7] or in a post-combustion capture unit at the gas stack of the reformer, where the CO_2 is separated from the exhaust gases using MEA absorption resulting in up to 90% CO_2 capture [8].

Natural gas is also the main feedstock for methanol production. Different plant layouts are considered depending on the plant size. Single-step reforming is mainly considered for plants up to 2500 MTPD (Metric Tons Per Day) capacity, while larger units (up to 10,000 MTPD) are based on a two-step reforming process, which features a combination of primary reforming (designed as an FTR) and oxygen-blown autothermal reforming using O_2 from a cryogenic air separation unit (ASU) [9]. The optimal syngas composition is reached when the so called module M (Eq. (5)) is equal to 2, which is the stoichiometric number required to reach the maximum CH_3OH yield.

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H_0^{298K} = -90.8kJ/mol \tag{3}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H_0^{298K} = -49.2kJ/mol \tag{4}$$

$$M = \frac{(H_2 - CO_2)}{(CO + CO_2)} \tag{5}$$

After cooling to nearly ambient temperature, the reformed syngas is compressed up to 50–100 bar in a multistage compressor, heated up to above 100 °C and fed to a cooled reactor operated at about 200–300 °C. The heat of reaction is released by producing intermediate pressure steam. The CH_3OH rich stream is cooled down, condensed and the liquid is separated from the unconverted gases, which are usually recirculated back to the methanol synthesis reactor. After that, the CH_3OH is sent to different separation columns to reach the required purity of 99.9% [2]. The conventional CH_3OH production process based on ATR reaches methanol yields of 0.82 mol_{CH3OH}/mol_{CH4} with about 0.17 kg_{CO2}/kg_{CH3OH} emitted to the atmosphere from the combustion of the process off-gases [10].

Among the several emerging solutions proposed for CO_2 capture in power plants and industrial processes [11], chemical looping technology represents one of the most promising and efficient alternatives, since the CO_2 separation is inherently integrated in the primary fuel conversion step [12]. If a metal oxide (named oxygen carrier) is alternatively exposed to air (for oxidation) and to a fuel stream (for reduction), a pure CO_2/H_2O stream is produced (chemical looping combustion, CLC). If a sub-stoichiometric OC-to-fuel ratio is adopted, partial fuel oxidation is obtained and reformate syngas can be produced (chemical looping reforming, CLR). CLR has been mainly studied using Ni-based oxygen carriers, which also present catalytic activity for the steam methane reforming reactions. Based on a simplified thermodynamic analysis it has been found that H_2 yields of 2.74 $molH_2/mol_{CH4}$ are achievable when working with a NiO/CH_4 molar ratio equal to 1.18 to sustain the endothermic reactions in the fuel reactor [13].

Due to the different catalytic activity and oxygen carrying capacity, different oxygen carrier materials have been considered for the CLR process [14]. Pröll et al. [15] have presented the performances of a dual circulating fluidized bed reactor operated with Ni/NiO as oxygen carrier in a 120 kW_{th} facility operated for >90 h, reaching >90% of methane conversion. Chiron et al. [16] have performed experiments and model validation in a micro packed-bed reactor (operated with 200 mg of oxygen carrier) and they have presented a reactor configuration in which the NiO supported on Al_2O_3 is reduced in a first stage and afterward used as catalyst in a second reactor where the SMR occurs. Ortiz et al. [13, 17,18] have presented both modelling and experimental demonstration of CLR in a 900 W_{th} fluidized bed unit. The experimental studies were carried out with a Ni-based catalyst and the process optimization has been undertaken by varying the steam-to-carbon ratio (S/C), the oxygen-to-carbon ratio (O/C or NiO/C), solid conversion (ΔX_s) and other relevant variables affecting the performance of the system. Different oxygen carriers have been synthetized and tested for CLR in fluidized bed configuration [19–21] and among all, the high reactivity of Ni for both fuel conversion and SMR results in the highest performances. However, the current high cost and toxicity compared with other oxygen carriers (OC) could hamper the use of Ni-based OCs. Moreover, the H_2 production process should preferably be carried out at high pressures, because industrial processes for CO_2 separation (through amine scrubbing) and purification (in a conventional pressure swing adsorption (PSA) unit or using membranes [22]) occur at high pressure and H_2 compression is extremely expensive from an energy point of view. This would involve the operation of CLR reactors under pressurized conditions, which is still unproven in circulating fluidized beds because the high pressure operation makes a stable circulation of solids and the loop seals rather challenging. A different approach for steam methane reforming have been proposed by Ryden et al. [23,24] in which the chemical looping reactor acts as combustion chamber to provide the heat of reaction to the reforming tubes which are immersed into the fuel reactor by converting the PSA-offgas into CO_2/H_2O inside the fuel reactor. In the last years, packed bed reactors (PBRs) have also been proposed for chemical looping combustion [25–28]. Diglio et al. [29] developed a 1D reactor model to simulate multiple cycles of a 22 cm long reactor with 6 cm diameter and presented the results of the cyclic process, where the reduction gas is first completely oxidized (gas-solid reactions) and thereafter the reformed syngas is produced.

In the present paper, chemical looping reforming in packed-bed reactors is tested and compared from an experimental and numerical point of view. With respect to the previous works on CLR, in the present work the OC reduction and reforming are not carried out in the same conversion step, but two different phases are distinguished. The proof of concept has been achieved in a lab-scale packed-bed reactor (3 cm of internal diameter, ID, and 1.5 m of reactor length) using Ni supported on $CaAl_2O_4$ as OC. The experimental demonstration focuses on the oxygen carrier stability under repeated reduction/reforming/oxidation phases for >400 h. A detailed reactor model is also discussed, which includes the estimation of the reactor heat losses and is validated with the experimental results. Finally, a large-scale reactor is designed and modelled for full scale applications for H_2 and CH_3OH production plants with integrated CO_2 capture.

2. Description of the concept and process integration

A schematic diagram of the CLR process with PBRs is presented in Fig. 1. Three main phases are carried out in sequence in three parallel reactors. The reactor operated in oxidation converts the Ni into NiO by reaction with the O_2 in the air stream while releasing N_2. The reactor operated in reduction, reduces the OC by using low grade fuel forming CO_2 and H_2O. Finally, a third reactor, in which the OC is in Ni form, is fed with natural gas together with recirculated CO_2/H_2O from the reduction phase and additional steam to convert CH_4 into syngas. The combination of CO_2/H_2O recirculation and additional H_2O is required to lower the H_2O consumption of the plant while keeping a very high CH_4 to H_2 conversion: in case only CO_2 is used, the reformate syngas is rich in CO and therefore more H_2O is required for the WGS reactions downstream of the CLR reactors; in case only H_2O (from the steam cycle) is used, relatively large quantities of H_2O are required to enhance the CH_4 conversion. Each reactor is operated sequentially in oxidation/reduction/reforming by switching the inlet gas streams. In order to avoid undesired mixing of the different reactants, a short purge cycle can be added before and after the oxidation.

In Fig. 2, a simplified plant flowsheet is depicted, illustrating a proposed process integration. After the reforming, the resulting syngas is cooled down to the desired temperature and sent to downstream plant units. In case of H_2 production, one or two conventional WGS