



## Full Length Article

## Steam reforming of shale gas with nickel and calcium looping

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## ABSTRACTS

High purity H<sub>2</sub> production from shale gas using sorption enhanced chemical looping steam reforming (SE-CLSR) was investigated at 1 bar, GHSV 0.498 h<sup>-1</sup>, feed molar steam to carbon ratio of 3 and 650 °C for 20 reduction-oxidation-calcination cycles using CaO and 18 wt% NiO on Al<sub>2</sub>O<sub>3</sub> as sorbent and catalyst/oxygen carrier (OC) respectively. The shale gas feedstock was able to cyclically reduce the oxygen carrier and subsequently reform with high H<sub>2</sub> yield and purity. For example H<sub>2</sub> yield of 31 wt% of fuel feed and purity of 92% were obtained in the 4th cycle during the pre-breakthrough period (prior to cycles with low sorbent capacity). This was equivalent to 80 and 43% enhancement compared to the conventional steam reforming process respectively.

## 1. Introduction

Hydrogen is regarded as the fuel of the future while worldwide demand for H<sub>2</sub> is expected to rise in both chemical and energy use [1]. Various processes for H<sub>2</sub> production such as partial oxidation, autothermal reforming, water electrolysis, biomass gasification and steam reforming have become commercially successful since it (H<sub>2</sub>) was discovered by Henry Cavendish in 1788. Catalytic steam reforming (C-SR) has emerged as the major technology for syngas production (in large scale) [2–6] in refining and petrochemical complexes [7] and steam methane reforming has become the most common method for large scale H<sub>2</sub> production for years [8]. Despite having reached technological and commercial maturity, the C-SR process is still one of the most energy intensive processes for syngas production through its heating requirement with high operational and maintenance cost [1,9]. To generate high purity H<sub>2</sub> and maximise yield, additional units such as water-gas shift (WGS) and separation units (such pressure swing adsorption, membrane or cryogenic technology) are included in a C-SR plant [10–12], making the process complex and economical only at large scales [11]. Global warming is presently one of the major concern in the world [13,14]. The C-SR process is also one of the contributors of global warming; by increasing the CO<sub>2</sub> concentration in the atmosphere. For every 4 mol of H<sub>2</sub> produced by complete steam methane reforming process for example, a mole of CO<sub>2</sub> is generated. In addition to tons of CO<sub>2</sub> generated [15] and release into the atmosphere by the reformer furnace flue gas. Thermodynamic constraints are also a major drawback of the process to date [16,17] requiring the process to be operated at high temperature, whilst medium-high pressures (30–40 bar) which thermodynamically limit the fuel conversion, have to be used to reduce

plant size. Other challenges of the process include risk of coke formation, limited catalyst effectiveness and overall the efficiency of the process has reached its maximum [18–20].

Researchers are presently focusing on novel technologies that generate H<sub>2</sub> at lower cost, eliminating or reducing the major remaining challenges with C-SR process. The development of technologies such as membrane reactor [21–25] permit C-SR reaction at mild operating conditions suppressing the thermodynamic limitations [10]. Similarly, coupling of C-SR with chemical looping usually termed Chemical looping steam reforming or ‘CL-SR’ [13,26–30] can minimise energy requirement, and sorption enhanced steam reforming (SE-SR) [31–35], as well as sorption enhanced chemical looping steam reforming (SE-CLSR) [6,36–42] combine H<sub>2</sub> production and CO<sub>2</sub> capture in a single reactor enhancing H<sub>2</sub> yield and purity compared to the conventional process, avoiding a separate water gas shift stage, and lowering the burden of H<sub>2</sub> separation. Membrane assisted SR, CLSR, SESR and SE-CLSR are all part of the current efforts in process intensification of H<sub>2</sub> production via reforming methods. The latter (SE-CLSR process) also minimises the energy requirement of operating the system to a great extent by close-coupling the heat demand of H<sub>2</sub> production with the heat released by the chemisorption of its CO<sub>2</sub> by-product. Detail process description with schematics of the SE-SR and SE-CLSR process can be found in S G Adiya et al. [9,43] and Ryden and Ramos [39].

Hydrocarbons are the major feedstock in steam reforming process for the generation of H<sub>2</sub> and synthesis gas [44]. Approximately, 90% of the global H<sub>2</sub> generated originates from conversion of fossil fuels [45]. A boom in shale gas production [13] and unconventional gas resources in the world such as hydrates foresees that gas will remain the main feedstock of steam reforming in the near term. The current

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development in oil and gas extraction such as drilling and fracking have made shale gas production economically viable [9]. Thus, additional techniques of gas consumption are also desirable due to its newfound albeit temporary abundance.

Presently, CaO is the best known natural solid high temperature CO<sub>2</sub> sorbent, and can be mined in the form of limestone (CaCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). Because of the sorbent's low cost, significant CO<sub>2</sub> sorption/desorption capacity even after repeated cycles, and fast reaction kinetics, CaO as high temperature CO<sub>2</sub> sorbent has attracted much attention. CaO's theoretical capture capacity of CO<sub>2</sub> is as high as 0.786 g of CO<sub>2</sub>/g of sorbent [46].

In the present study, experimental analysis of hydrogen production via the SE-SR and SE-CLSR processes using a model composition shale gas with CaO<sub>(s)</sub> sorbent and NiO based catalyst / oxygen carrier (OC) was conducted on a bench scale packed bed reactor for the first time. This follows from our previous study (S G Adiya et al. [47]) which focused on the same materials and feedstock (NiO based catalyst / oxygen carrier (OC) and shale gas) and assessed via experiments the steam reforming of shale gas with and without chemical looping. The purpose of the study is to demonstrate the effect of coupling sorption enhancement (SE) and chemical looping (CL) in C-SR process in packed bed reactor using a realistic feedstock, as well as validate our previous thermodynamic equilibrium analysis in S G Adiya et al. [9].

## 2. Materials and methodology

### 2.1. Experimental materials

The model shale gas mixture used for the experiment was reproduced from cylinders of different hydrocarbons. The desired molar composition (Table 1) was calculated based on the mole fraction of the species and a given total volumetric flow rate selected according to desired gas hourly space velocity (GHSV). A detailed description of the experimental materials and rig set-up can be found in the Supplementary data (SD1 and SD2) and was described in a previous publication [47]. CaO sorbent and commercial 18 wt% nickel oxide on aluminium oxide support (NiO on Al<sub>2</sub>O<sub>3</sub> support) catalyst was provided by Twigg Scientific & Technical Ltd for the experimental study. The catalyst performed the dual action of catalyst and OC.

### 2.2. Experimental procedure

2 g of catalyst and 1 g of CaO sorbent (1.2 mm mean size) were loaded into the reactor before setting up the experimental rig as described in SD2. The catalyst particle size was chosen to respect the particle-reactor diameter ratio (ca. 1/10) found in industrial SMR plants where diffusion as well as kinetic limitations control the reaction rates, while maintaining low pressure drop between reformer inlet and outlet and offering good mechanical strength. After setting the experimental rig, the furnace temperature was then set to the desired temperature e.g. 650 °C This was followed by reduction of the catalyst from non-active NiO to catalytically active Ni phase, conducted using a gas mixture feed of 5 vol% hydrogen in nitrogen carrier gas. The nitrogen and hydrogen flow rate were 200 and 10 cm<sup>3</sup> min<sup>-1</sup> (STP) respectively. Reduction of the NiO to Ni resulted in micro GC H<sub>2</sub> vol. % reading which remained at zero, and then returned to 5 vol% after about

**Table 1**  
Composition of shale gas used for experiments [48].

Species	Composition (%) [48]	Molar flow (mol/s)
CH <sub>4</sub>	79.4	$2.68 \times 10^{-6}$
C <sub>2</sub> H <sub>6</sub>	16.1	$5.44 \times 10^{-7}$
C <sub>3</sub> H <sub>8</sub>	4.0	$1.35 \times 10^{-7}$
N <sub>2</sub>	0.4	$1.35 \times 10^{-8}$
Total	100	$3.37 \times 10^{-6}$

45 min, indicating that the catalyst had completed its reduction step. Hydrogen flow was then stopped, leaving only the nitrogen feed until the hydrogen reading reached 0% again, having flushed out all the reducing H<sub>2</sub> from the reactor. This was followed by the SE-SR process, which started by feeding water and fuel (shale gas) to the reactor using the programmable syringe and MKS flow controller respectively at the desired molar steam to carbon ratio. Experiments lasted for at least 3 h and ended by turning off the water and fuel flows first, then the furnace. This left only nitrogen feed to completely flush out the reformat gases and cool down the reactor before turning off the chiller and dismantling the rig for the next experiments when the reactor temperature had reached ambient temperature.

The experimental procedure for the first cycle of SE-CLSR process was exactly the same as that of the SE-SR process procedure (above). In both processes an air feed of 500 cm<sup>3</sup> min<sup>-1</sup> STP and 850 °C had the effect of simultaneously re-oxidising the catalyst/OC, and regenerating it by also burning off any carbon that might have deposited on the catalyst/OC. The choice of higher oxidation temperature of 850 °C was to fully regenerate the sorbent (CO<sub>2</sub> desorption by calcination). The recorded temperature during air feed increased by roughly 10–15 °C owing to the oxidations reactions of the carbon residue and re-oxidation of the nickel-based catalyst. The major difference between the experimental procedures of the SE-CLSR process and those of the SE-SR process was the presence of the reducing H<sub>2</sub>/N<sub>2</sub> feed in the SE-SR process, whereas the SE-CLSR process relied on autoreduction of the catalyst. The experimental procedure for C-SR process used for comparison was also exactly the same as that of the SE-SR process except that 3 g of catalyst on its own was used in the C-SR process as opposed to the 2 g of catalyst and 1 g of CaO in both the SE-SR and SE-CLSR processes. The choice of 2 g of catalyst in the SE- processes was a compromise between increasing the reactor bed load and increasing the gas input to maintain the same gas hourly space velocity when comparing the conditions with and without Ca sorbent. The latter, which resulted in a higher carbon input, was considered less logical. A full description of the post processing procedures allowing the calculations of water conversion, H<sub>2</sub> purity and molar yields of products can also be found in SD3. Explanation of thermodynamic methodology and characterisation techniques used can be found in SD4 and 5 respectively and are also described in [47].

## 3. Results and discussion

### 3.1. Sorption enhanced steam reforming (SE-SR) process of shale gas

#### 3.1.1. Effect of temperature on SE-SR process

Temperature is one of the major variables on which the conversion of CaO and its carbonation capacity is determined. The effect of temperature on sorption enhanced steam reforming (SE-SR) process was investigated from 600 to 700 °C at GHSV 0.498, 1 bar pressure and feed molar steam to carbon ratio (S:C) of 3 using CaO as CO<sub>2</sub> sorbent. Higher temperature during sorption were not investigated as they owing to the thermal decomposition of CaCO<sub>3(s)</sub> [9,49–51]. Moreover, the equilibrium vapour pressure of CO<sub>2</sub> over CaO<sub>(s)</sub> is low at low temperatures [9,39,52]. Consequently, only the range of 600–700 °C was investigated. Lower temperatures were not investigated either because they suppressed catalyst activity.

Table 2 presents the plots of average values of H<sub>2</sub> yield and purity over temperature range. H<sub>2</sub> yield and purity decreased gradually as temperature increased. This was expected because the SE process is favoured at low/medium temperature [38] for reasons explained earlier. The conversion of feedstocks (fuel and H<sub>2</sub>O conversion) were not reported during the carbonation period because equations they are derived from were not applicable due to the inability to quantify the carbonation rate on the solid sorbent at any given time. However, gas yields including that of H<sub>2</sub> were quantifiable using the nitrogen balance.

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