

# Production of hydrogen by unmixed steam reforming of methane

V. Dupont<sup>a,\*</sup>, A.B. Ross<sup>a</sup>, E. Knight<sup>a</sup>, I. Hanley<sup>a</sup>, M.V. Twigg<sup>b</sup>

<sup>a</sup>Energy and Resources Research Institute, University of Leeds, Leeds LS2 9JT, UK

<sup>b</sup>Johnson Matthey Plc, Orchard Road, Royston SG8 5HE, UK

Received 5 July 2007; received in revised form 20 December 2007; accepted 6 February 2008

Available online 16 February 2008

## Abstract

Unmixed steam reforming is an alternative method of catalytic steam reforming that uses separate air and fuel–steam feeds, producing a reformat high in H<sub>2</sub> content using a single reactor and a variety of fuels. It claims insensitivity to carbon formation and can operate autothermally. The high H<sub>2</sub> content is achieved by in situ N<sub>2</sub> separation from the air using an oxygen transfer material (OTM), and by CO<sub>2</sub> capture using a solid sorbent. The OTM and CO<sub>2</sub> sorbent are regenerated during the fuel–steam feed and the air feed, respectively, within the same reactor. This paper describes the steps taken to choose a suitable CO<sub>2</sub>-sorbent material for this process when using methane fuel with the help of microreactor tests, and the study of the carbonation efficiency and regeneration ability of the materials tested. Elemental balances from bench scale experiments using the best OTM in the absence of the CO<sub>2</sub> sorbent allow identifying the sequence of the chemical reaction mechanism. The effect of reactor temperature between 600 and 800 °C on the process outputs is investigated. Temperatures of 600 and 800 °C under the fuel–steam feed were each found to offer a different set of desirable outputs. Two stages during the fuel–steam feed were characterised by a different set of global reactions, an initial stage where the OTM is reduced directly by methane, and indirectly by hydrogen produced by methane thermal decomposition, in the second stage, steam reforming takes over once sufficient OTM has been reduced. The implications of these stages on the process desirable outputs such as efficiency of reactants conversion, reformat gas quality, and transient effects are discussed. Crown Copyright © 2008 Published by Elsevier Ltd. All rights reserved.

**Keywords:** Hydrogen; Methane; CO<sub>2</sub> sorbent; Oxygen transfer; Reforming; Carbon

## 1. Introduction

Unmixed steam reforming, henceforth called ‘USR’, first appeared in the mainstream scientific literature through the two publications Kumar et al. (1999) and Lyon and Cole (2000). It offers an alternative method for the autothermal production of a hydrogen-rich reformat (more than 90% dry). It relies on alternated feeds of air and of a mixture of vapourised fuel and steam to create a cyclic process. During USR, the fuel–steam feed and the air feed do not mix, contrary to conventional autothermal catalytic steam reforming, where pure oxygen is relied on for partial oxidation of the fuel and providing heat for the endothermic steam reforming reaction. Instead, the USR process makes use of an oxygen ‘mass transfer’ material or OTM, here chosen to be reduced nickel supported on alumina. Although various reactor and flow configurations are possible

with USR, a plug flow fixed bed reactor is used in the present study, where the bed materials are crushed to 1–2 mm size. The OTM is able to store oxygen exothermically by forming the NiO on the support when subjected to an air flow, thus heating up the reactor bed evenly over its cross-section, and allowing the inert N<sub>2</sub> component to evolve separately from the reformat. The oxide then regenerates to metallic Ni by reduction when it is exposed to the subsequent fuel and steam feed, responsible for the main steam reforming reaction. When a CO<sub>2</sub>-sorbent material is used in combination with the OTM, the catalytic reaction of steam reforming proceeding under the fuel–steam feed on the hot Ni–OTM catalyst bed occurs alongside CO<sub>2</sub> capture. This results in further purification of the reformat as well as favouring the water gas shift reaction towards H<sub>2</sub> production. The reformat can reach more than 90% content in H<sub>2</sub> (dry) as a result of the combined in situ N<sub>2</sub> and CO<sub>2</sub> separations and the increased WGS. Some of the heat liberated under the following air flow is then utilised to decompose the carbonate present, thereby regenerating the CO<sub>2</sub> sorbent for the

\* Corresponding author.

E-mail address: v.dupont@leeds.ac.uk (V. Dupont).

next cycle while the Ni–OTM oxidises. The evolutions of CO, CO<sub>2</sub>, and H<sub>2</sub>, proceed under the fuel–steam feed. Under air feed, the reactor effluent is an oxygen-depleted and CO<sub>2</sub>-laden air stream. When using one fixed bed reactor, the production of hydrogen is therefore intermittent. For the process to continuously produce hydrogen, two identical reactor beds would need to run in parallel, each operating in a different half cycle. Alternative ways of continuously producing H<sub>2</sub> with a single reactor could also involve the use of a rotating bed travelling through air feed then fuel–steam feed zones. USR has previously been demonstrated using methane and diesel fuels (Kumar et al., 1999; Lyon and Cole, 2000). Over subsequent years, DOE reports and conference presentations appeared in the literature as research and development continued from the original work and the terminology of autothermal cyclic reforming (Kumar et al., 2004), as well as unmixed fuel processing were also used in this context (Zamansky, 2002; Rizeq et al., 2003). Close relatives of USR are chemical looping combustion (Ishida et al., 1987; Son and Kim, 2006), and coal hybrid combustion–gasification chemical looping (current work by the US’ DOE National Energy Technology Laboratory).

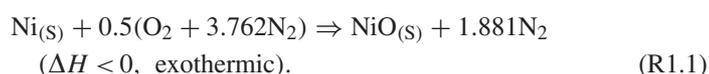
A number of advantages are claimed for the USR process: (i) production of H<sub>2</sub>-rich reformat (ca. 90% dry H<sub>2</sub>) with a single reactor, (ii) potential for autothermal operation without the need for pure oxygen that would require a costly air separator pre-processing stage, (iii) improved heat transfer characteristics that allow down-scaling up of the process to a point, increasing its potential for distributed power generation if coupled with an intermediate temperature solid oxide fuel cell, or with a molten carbonate fuel cell, (iv) low cost reactor materials due to a hotter reactor centre and colder walls, (v) compactness of the process due to coupling of the endothermic and exothermic reactions within the reactor rather than relying on external heating, (vi) separation of CO<sub>2</sub>-containing effluent from the H<sub>2</sub>-rich reformat with potential for cheaper purification downstream technologies, (vii) insensitivity to coking, (viii) insensitivity to sulphur (as claimed by Lyon and Cole, 2000), finally, and related to the last two points, (ix) fuel feedstock-flexibility (gas and liquid). Currently there are adaptations of the principle of USR to pulverised coal using circulating fluidised bed technologies which draw similarities with chemical looping combustion (Rizeq et al., 2003).

The cycle of reactions involved in the methane unmixed reforming process is shown below and includes some reactions that were identified during the present investigation in addition to those mentioned in the literature.

### 1.1. First half of cycle: air feed

The main reactions are

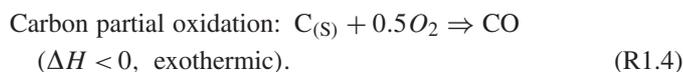
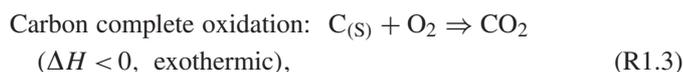
Oxidation of the supported OTM and separation of N<sub>2</sub> from air:



Reaction (R1.1) heats up the OTM’s bed and some of its heat is used in the regeneration of the CO<sub>2</sub> sorbent:



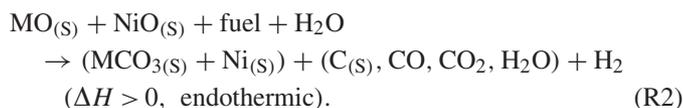
In addition to Reactions (R1.1) and (R1.2), identified in Lyon and Cole (2000) as the reactions at work under air flow, Reactions (R1.3) and (R1.4) were found to play a significant role during the present work:



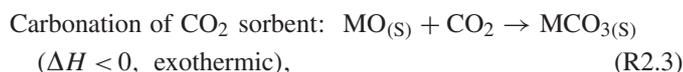
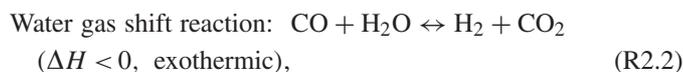
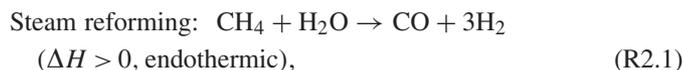
The gas product from this half cycle is N<sub>2</sub> rich containing CO<sub>2</sub> and unreacted O<sub>2</sub>.

### 1.2. Second half of cycle: fuel–steam feed

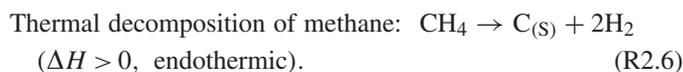
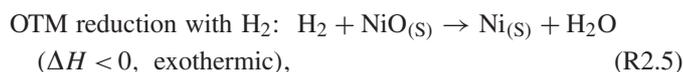
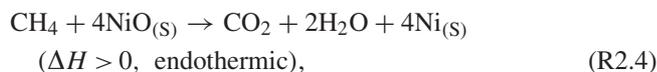
The vapourised fuel and steam mixture encounters the hot reactor bed and the following global reaction occurs:



Reaction (R2) is the overall reaction, it can be split up into the global reactions below:



OTM reduction with methane (unmixed combustion of methane):



The main mechanism of unmixed reforming is illustrated in Fig. 1.

Similar processes such as chemical looping combustion and sorption-enhanced gasification or reforming in circulated fluidised beds offer similarities of chemical mechanism to unmixed combustion, although these terms seem to have been so far applied to interconnected fluidised or circulating beds through which the OTM and/or the CO<sub>2</sub> sorbent circulate undergoing redox or absorption/desorption stages. Since the birth of chemical looping combustion (Richter and Knoche, 1983;

Download English Version:

<https://daneshyari.com/en/article/158209>

Download Persian Version:

<https://daneshyari.com/article/158209>

[Daneshyari.com](https://daneshyari.com)