Fuel 118 (2014) 100–106

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Purified hydrogen from synthetic biogas by joint methane dry reforming and steam-iron process: Behaviour of metallic oxides and coke formation

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HIGHLIGHTS

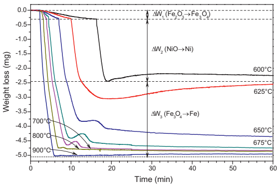
- Production of purified hydrogen starting from synthetic biogas by joint MDR and steam-iron.
- Low heating power biogas has been simulated by equimolar mixtures of CH_4 and CO_2.
- Solid composed of nickel catalyst and doped iron ores as reactive material.
- TG + MS to determine relation between exhaust gas and mass gain/loss of solid.
- Insight over reactions sequence, carbon deposition and self-gasification.

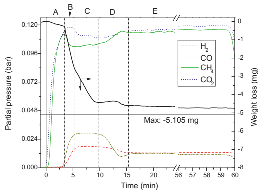
ARTICLE INFO

Article history:
Received 23 July 2013
Received in revised form 18 October 2013
Accepted 29 October 2013
Available online 8 November 2013

Keywords:
Biogas
Dry-reforming
Steam-iron
Hydrogen
Chemical-looping

GRAPHICAL ABSTRACT





ABSTRACT

Mechanical mixtures of nickel oxide and iron oxide doped with small quantities of ceria and alumina (2 wt%), have been tested as suitable solids to jointly produce and purify hydrogen from an equimolar mixture of CH_4 and CO_2 simulating a desulfurized biogas. Since the solid mixture constitutes a reactant within the system, most part of the experiments has been carried out in a thermogravimetric system acting as a differential reactor. Exhaust gases were continuously monitored by mass spectrometry at the exit of the thermobalance. The apparent reaction mechanism consists of a first stage in which CH_4 reduces Fe_2O_3 (hematite) to Fe_3O_4 (magnetite) and NiO to metallic Ni. This newly formed metallic nickel adopts a catalytic role promoting the methane dry reforming (MDR) reaction between CH_4 and CO_2. Fe_3O_4 reduces to metallic iron (Fe^0) at the expense of H_2 and CO (products of MDR), that transform in the oxidized species H_2O and CO_2 respectively. This reaction displaces dry reforming towards products what avoids carbon formation at some extent. Carbon deposition has been detected at temperatures lower than 900 °C. These deposits were partially removed along isothermal experiments, probably by CO_2 (Boudouard), and/or newly formed H_2 and CO (MDR). EDS analysis demonstrated that carbon is mostly formed on the surface of nickel particles, while Raman spectroscopy shows that this carbon was highly graphitized. Metallic iron can be reoxidized with steam in a subsequent stage releasing high purity hydrogen.

1. Introduction

As time goes by energy supply becomes an issue of capital importance worldwide. Currently, most of the energy around the world is still produced from fossil fuels, constituting a non-suitable environmental choice and a questionable bet in a mid and long term future. In this context, hydrogen is rising as a promising alternative to diminish greenhouse emissions and accordingly the climate change; not only because it does not contribute to the carbon fingerprint if produced from renewable sources, but

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0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.10.069

because if fed to fuel cells, constitutes an energy vector in transport, one of the most polluting sectors [1].

Several methods are being employed in current hydrogen production. Steam reforming of natural gas followed by purification by pressure or temperature swing adsorption (PSA and TSA) is widely used due to the fact that it is a cheap and mature technology [2]. Coal gasification also falls in the category of proven technologies but with an important drawback regarding its polluting effect [2].

Water electrolysis seems to be a promising alternative provided that electricity needs are covered by renewable sources like solar or wind mill farms during off-peak times. Although the high purity achievable by this method makes it very suitable for PEMFC (e.g. transport and allocated applications), its high price makes this alternative uncertain up to date [2–4].

Thermocatalytic decomposition of methane (natural gas), is another alternative with which high value by-products like carbon nanofibers and nanotubes are foreseen to be co-produced [5]. Other alternatives plan obtaining hydrogen starting from biomass via gasification or pyrolysis [2,6–8]. All of these promising options bear in mind two important aspects: the renewable origin of the source, and the high purity of hydrogen to be achieved. In this sense, the present work is intended for exploring new ways of generation of pure hydrogen starting from another alternative biomass source: biogas [9].

Biogas is produced by the anaerobic digestion of organic matter, such as biomass, municipal solids, and industrial or livestock wastes [10]. Its composition includes mainly CH_4 and CO_2 which accounts for up to 98(vol%) depending on the source [11]. Nitrogen, hydrogen sulphide, siloxanes and steam are also present but in minor proportions [10–12]. Currently the most used method to take profit from this gas consists of burning it in internal combustion engines producing electricity and heat by cogeneration. Taking apart minor components like H_2S and siloxanes that must be removed prior to almost any further treatment, among the main drawbacks for such use can be mentioned the low heating value of the biogas [10] and the knocking properties that might mechanically damage the engines depending on the CH_4/CO_2 ratio [13]. On the other side, methane dry reforming (MDR) seems to be an interesting alternative since taking apart the above mentioned contaminants, the CH_4/CO_2 ratio of the mix can be profitable for producing rich mixtures of H_2 and CO. In this case, an unavoidable task is the further purification of the hydrogen contained in the mixture if it is going to be post-processed in a PEMFC. Moreover, an important drawback of this reaction, pointed out recently by Oyama et al. [14], is that carrying out the reaction at pressures only slightly above atmospheric (5 bar), reverse water gas shift can be drastically promoted, consuming the incipient hydrogen and carbon dioxide to produce carbon monoxide and water. An ideal solution would consist of removing hydrogen as soon as it is produced, substituting it by steam.

To cope with these issues, two coupled processes are being proposed in this work: on the one hand, the catalytic dry reforming of methane [15]. On the other, the steam-iron process originally devoted to produce pure hydrogen for aerial navigation in the early XX century from mixtures resulting from coal gasification [16,17].

Steam-iron process consists ideally of two steps occurring in a cyclic and discontinuous manner. The reduction of iron oxides with a reductive gas to obtain metallic iron or iron in a lower oxidation state (r.1) and (r.2) constitutes the first stage. The second stage consists of the reoxidation of the previously reduced iron with steam (r.3). Hydrogen is then released and iron oxide is regenerated completing the cycle. Several applications as hydrogen production [18,19], hydrogen purification [20,21] and hydrogen storage [22] are possible depending on the composition of the reductive gas.

$$Fe_2O_3 + 3H_2 \rightleftharpoons 2Fe + 3H_2O \tag{r.1}$$

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2 \tag{r.2}$$

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2 \tag{r.3}$$

In this context, sweetened biogas can behave as reductive source depending on its CH_4 to CO_2 proportion. Nevertheless, methane alone is not able to reduce iron oxide to metallic iron at moderate temperatures (e.g. 500–650 °C) because of thermodynamic limitations [23]. To afford this task it is necessary to favour methane dry reforming (r.4) with the aid of a catalyst which produces H_2 and CO that actually are the potential reducers of iron oxides [24,25]. Since this reaction follows a comparable path to that of steam reforming, same kind of catalysts can be considered to undertake this job [26].

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{r.4}$$

According to these authors, the reaction mechanism consists of two steps. The first one corresponds to methane dehydrogenation (r.5), being the second one the gasification of the previously deposited coke by CO_2 (r.6). In both cases the reaction takes place in the surface of the metallic nickel [27].

$$Ni(s) + CH_4 \rightleftharpoons Ni - C(s) + 2H_2 \tag{r.5}$$

$$Ni - C(s) + CO_2 \rightleftharpoons Ni(s) + 2CO \tag{r.6}$$

The most widely used catalyst to carry out this task is nickel supported on alumina. Although metallic iron from reactive solid could act as catalyst, its effect is negligible at the temperature range tested [5]. Nickel crystallites size and dispersion degree along the catalyst surface are key factors in its performance [28]. These characteristics also influence the type and reactivity of the coke eventually formed. Chen et al. [29] established that the higher the size of crystallites, the less probable is the formation of carbon nanotubes or nanofibers, allowing on such way the appearance of important quantities of amorphous carbon that could be more easily gasified than those highly structured. An adequate control of the size of nickel crystallites can lead to a convenient balance between simultaneous coke production and gasification, during dry reforming of biogas. Bulk catalyst based in nickel oxides, with crystallites in the order of hundred microns can be a good candidate.

The main objective of this work has been testing the feasibility of producing as purer hydrogen from a sweetened biogas as could be achieved, by the joint action of two processes taking place in the same reactor. Catalytic methane dry reforming – MDR – (r.4) produces hydrogen which is sequestrated by reducing an iron based oxide (steam-iron) (r.1). Same role plays CO co-produced with H_2 (r.2). After reduction, hydrogen can be released in a further stage by reaction of the metallic iron with steam according to reaction (r.3).

2. Experimental

2.1. Materials

Solid was composed of a mechanical mixture of a reactive one (iron oxide plus additives) and a catalyst (nickel oxide). The composition of the first is the result of a previous research focused on purification of methane pyrolysis gases by the steam-iron process [30,31]. Its main component is Fe_2O_3 (hematite) (98 wt%) which is doped with 1.75(wt%) of Al_2O_3, that stabilizes its mechanical properties and 0.25(wt%) of CeO_2 that promotes its reactivity.

Solids were synthesized separately according to a precipitation method based on citrates [32]. The starting materials were