



Biogas reforming using renewable wind energy and induction heating



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ARTICLE INFO

Article history:

Received 28 February 2014

Received in revised form 25 May 2014

Accepted 3 June 2014

Available online 19 July 2014

Keywords:

Biogas

Induction heating

Reforming

Perovskites

Wind power

ABSTRACT

While the benefits of renewable energy are well known and used to influence government policy there are a number of problems which arise from having significant quantities of renewable energies on an electricity grid. The most notable problem stems from their intermittent nature which is often out of phase with the demands of the end users. This requires the development of either efficient energy storage systems, e.g. battery technology, compressed air storage etc. or through the creation of demand side management units which can utilise power quickly for manufacturing operations. Herein a system performing the conversion of synthetic biogas to synthesis gas using wind power and an induction heating system is shown. This approach demonstrates the feasibility of such techniques for stabilising the electricity grid while also providing a robust means of energy storage. This exemplar is also applicable to the production of hydrogen from the steam reforming of natural gas.

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1. Introduction

Greener sources of energy are continually being investigated as alternatives to fossil fuels and of these, biogas which is derived from the anaerobic digestion of biomass, is interesting from both a financial and environmental viewpoint. Biogas is a secondary energy carrier which can be manufactured from a range of organic materials resulting in the production of methane that can be used for the generation of on-site energy or potentially through gas to liquid processes (GTL) to methanol, dimethyl ether (DME) or higher hydrocarbons by Fischer–Tropsch processes [1,2].

As the main components of natural biogas are methane (55–70% in volume) and carbon dioxide (30–45% in volume) with ppm levels of H₂S, NH₃, H₂, N₂, O₂ and H₂O [3], scrubbed mixtures of this are thus suitable feed for the dry reforming of methane (DRM) reaction (CH₄ + CO₂ ↔ 2CO + 2H₂, ΔH° = 247 kJ mol⁻¹).

Dry reforming of methane represents the lowest cost route to the production of syngas [4] from biogas whereas steam reforming (CH₄ + H₂O ↔ CO + 3H₂, ΔH° = 206 kJ mol⁻¹) is the most industrially applied catalytic process used to date [5].

The main obstacle to the industrial implementation of DRM is the absence of commercial catalysts with a proven high activity and stability and a resistance to carbon accumulation [6]. The most active metals for the DRM are those from groups 8, 9 and 10 with

Ni being the most commonly used because of its availability and price [7]. Recent studies have focused on the development of complex mixed metallic oxides with a perovskite structure as they are suitable for methane conversion in reactions such as steam reforming, partial oxidation and dry reforming. It has been reported that the perovskite-type oxides precursors fulfil the requirements of high metal dispersion and thermal stability in the dry reforming of methane [8]. The utilization of ABO₃ perovskites oxides, where the A-site cation is a rare earth and/or alkaline earth, and the B-site cation is a transition metal, has increased lately [9]. A common structure for DRM is LaNiO₃ and it has been found that the addition of alkali metals or rare earth elements helps reduce carbon deposition [10,11] while the dilution of Ni in the metallic particles by a second metal such as Mn, Fe, Cu, or Al helps prevent sintering [12]. A perovskite-type mixed metal oxide material with the composition Na_{0.5}La_{0.5}Ni_{0.3}Al_{0.7}O_{2.5} is one such catalyst which has shown very good performance [13]. This particular catalyst forms the basis of the work herein and was selected from a range of previously tested catalysts the results of which are not included here.

As discussed above this reaction is highly endothermic and thus requires a significant energy input. Conventional heating using standard furnaces results in slow start-up times due to the overall heat capacity of the system. While this has certain advantages it is considered to be too slow in order to adjust to the changes in wind speed which this paper is targeting. Hence the feasibility of energising the reaction by induction heating will be shown.

This method can also be used as a strategy for lowering carbon rates and improving stability when compared to traditional heating

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systems [14,15]. According to theory, three types of electromagnetic heating can be described depending on the frequency of the electromagnetic field used: (a) induction heating (IH) or radiofrequency (RF), (b) dielectric or (c) microwave [16]. IH presents the lowest frequency being in the range of 1000 Hz which presents several advantages as it is not harmful to human body and is uniform and this flexibility gives the possibility of adapting it to renewable energy fluctuations. For example IH has shown its ability to quickly and homogeneously heat metallic surfaces [17] similar to the stainless steel reactor is used in the present work.

To our knowledge induction heating has never been applied to the dry reforming of methane reaction before and its direct application in combination with wind power is described in this paper. While IH techniques for the DMR are considered novel Dieckmann [14] has previously demonstrated an enhanced performance of a Ni-based catalysts for diesel reforming using electromagnetic fields, reporting an approximate 4 fold reduction in the carbon formation.

When studying the dry reforming of methane, coke formation and catalyst deactivation must be considered and keeping these two issues under control is critical for long term operation. Additionally the reverse water gas shift (RWGS), methanation reaction and steam reforming of methane may also affect the equilibrium [18,19]. Hence the effect of IH on the catalyst stability as well as product distribution is important.

2. Experimental

2.1. Preparation of perovskite catalytic precursors

A sol-gel method was applied to prepare the mixed-oxide $\text{Na}_{0.5}\text{La}_{0.5}\text{Ni}_{0.3}\text{Al}_{0.7}\text{O}_{2.5}$ [13] used in the induction heating experiments. Initially precursor solutions were prepared by dissolving the raw materials in previously heated propionic acid. The precursor reagents; lanthanum nitrate hexahydrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, aluminum nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and sodium nitrate NaNO_3 were separately dissolved in the minimum volume of hot propionic acid at atmospheric pressure and 90 °C. All reagents had a purity >99% and were supplied by Sigma-Aldrich Ltd. After dissolution, each solution was mixed and stirred at atmospheric pressure and 130 °C for 120 min. After that, the propionic acid was distilled in a reflux process until the formation of a gel was observed, which was dried at 90 °C overnight and then calcined in a static air atmosphere at 725 °C for 4 h. After calcination, the catalyst was tested.

2.2. Experimental setup

A system using a feed composed of a mixture of methane and carbon dioxide, i.e. the main components of natural biogas was used. The dry reforming tests were carried out with a synthetic mixture of $\text{CH}_4:\text{CO}_2:\text{Ne}$ in a ratio of 9.5:9.5:1 with a GHSV of $30,000 \text{ cm}^3 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ when using the gas chromatographer for analysis of the gas outlet or with a mixture of $\text{CH}_4:\text{CO}_2:5\% \text{ Kr/Ar}$ in a ratio of 9.5:9.5:1 when using the mass spectrometer for analysis of the gas outlet. The total flow used was 50 mL min^{-1} . This is a suitable approximation to natural biogas while allowing for an inert gas (Ne or Kr) to be used for calibration. All gases were supplied by BOC and had greater than 99% purity.

The bed of catalyst was set up with 0.1 g of catalyst, in the form of 250–425 μm diameter pellets and was placed in the centre of the stainless steel reactor (inner diameter of 6.35 mm) and secured with quartz wool at both sides in order to prevent movement of the catalyst during reaction.

A schematic diagram of the system is shown in Fig. 1. Here a 2 kV Ambrell Easyheat unit (Fig. S1) was used to produce the induction heating through a 9-turn copper solenoid coil applicator. Cooling water was used inside the coil at 20 °C. The stainless steel fixed bed reactor was situated inside the induction coil. The gases were fed into the reactor and the products analysed by an on-line gas chromatograph (GC) and/or mass spectrometer (MS) where appropriate. The GC utilised was a Perkin Elmer Clarus 500 provided with a Hayesep DB column and equipped with FID and TCD detectors. A quadrupole MS Hiden™ HPR-20 operated by MASsoft software was also used. A post reaction temperature programme oxidation (TPO) was performed using the MS and a Carbolite® furnace model MTF 10/25/130, this was done *in situ* in the stainless steel reactor. After the reforming reaction, the sample was not taken out, but the inlet and outlet of the reactor were disconnected to remove the induction coil. The coil was then substituted by the Carbolite® MTF 10/25/130 furnace. The outlet of the reactor was connected to the mass spectrometer for the analysis of the gas products. For the temperature programmed oxidation experiments typically, 2, 15, 16, 18, 20, 22, 28, 32, 44, 82, and 84 amu were followed while for the catalytic experiments 13, 28, 44, 82 and 84 amu were registered.

The TPOs were conducted from room temperature to a maximum of 800 °C using a heating ramp of 5 °C/min. The feed used was 50 mL min^{-1} of total flow in a ratio of 20% O_2/Ar : 5% Kr/Ar : $\text{He} = 2.5:1:1.5$, this is 25 mL min^{-1} of 20% O_2/Ar , 10 mL min^{-1} of 5% Kr/Ar (using Kr as internal standard for the TPO) and balanced with He (15 mL min^{-1}).

The completed 2 kV Ambrell Easyheat unit used to provide the electromagnetic field and the system operating under biogas reforming is shown in the supplementary information. The reaction temperature was measured using a high speed fibre optic infrared transmitter OS4000 from Omega UK which operates in the temperature range from 300 to 1200 °C. It was positioned such that no contact with the reactor took place and the signal was recorded online using the OMEGASOFT™ infrared temperature software interface. In order to provide additional temperature data inside the reactor, a K-type thermocouple supplied by Omega UK was used. This temperature was also recorded online using the PicoLog data acquisition software under reaction conditions. Figures of the real system set up used are shown in the supplementary information (Figs. S1 and S2).

When steam reforming of methane experiments were performed, slight modification of the rig to allow the introduction of steam in the feed of gases was required. The steam reforming experiment was carried out with an S/C ratio of 1.1 to allow all the methane to be converted. The total flow rate used was 50 mL min^{-1} with 5% of internal standard (Ne or 5% Kr/Ar) depending if GC or MS was used. Methane and the internal standard were fed through a saturator whose temperature was controlled by a Grant™ GP 200 thermostatic bath. All the gas lines from the mass flow controllers to just before the induction system and after the outlet of it to the GC/MS entrance were heated to prevent water condensation using regulators controlled by tapes from Barnstead-Electrothermal™.

2.3. Characterisation of the mixed metallic oxides

X-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX/EDS), analysis, Brunauer-Emmett-Teller Analysis (BET) and scanning electron microscope (SEM) measurements were used over the fresh and used samples.

The XRD analysis was carried out using a PANalytical Xpert-Pro equipment, which operates at 40 kV and 40 mA, using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). Xpert data viewer software was used in conjunction with the instrument.

The SEM used was a FEI Quanta 250 FEG MKII with a high resolution environmental microscope (ESEM) using XT microscope

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