Plasma-catalytic reforming of methane for hydrogen production at low temperatures

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The rapid exhaustion of fossil fuel reserves and the adverse effects of climate change caused by increasing global energy demands have attracted great attention and pose serious threats to humankind. The emergence of clean energy technologies is crucial and essential to reduce the negative effects of climate change and to ensure global energy security based on sustainable and renewable energy sources. Dry reforming of methane and carbon dioxide has recently attracted significant interest due to simultaneous production of hydrogen and reduction of two abundant greenhouse gases. However, one of the main challenges of thermal catalytic reaction is the high energy/strength of the C-H bond, requiring high temperature to break it and incurring a high energy cost. In addition, the formation of carbon deposition will cause rapid deactivation of the catalysts, especially for non-noble catalysts.

Non-thermal plasma technology provides an attractive alternative to the conventional catalytic route for the conversion of greenhouse gases into value-added fuels. In non-thermal plasmas, the overall gas temperature can be as low as room temperature, while the electrons are highly energetic with a typical temperature of 1-10 eV, which is sufficient to breakdown inert molecules and produce highly reactive species such as free radicals, excited atoms, ions and molecules, enabling thermodynamically unfavourable reactions to occur at atmospheric pressure and low temperatures. High reaction rate and fast attainment of steady state in plasma process allows rapid start-up and shutdown of the process compared to other thermal treatment, which significantly reduces the energy cost and offers a promising H2 production route for applications. Another distinguish advantage of plasma technology is its ability to be combined with other technologies such as catalysis, known as plasma-assisted catalysis. The use of plasma in combination with solid catalyst has the potential to enhance the conversion of feed gases, improve the selectivity toward the desired products and to reduce the operating temperature of the catalyst which both increases the energy efficiency of the process and improves the stability of the catalysts, as evidenced by a synergistic effect.

In this work, a coaxial dielectric barrier discharge (DBD) plasma reactor has been developed for the plasma-catalytic chemical reactions at low temperatures (< 250°C). The integration of plasma and supported Ni catalyst (Ni/Al2O3) clearly exhibits a significant synergistic effect, showing both the conversion of feed gases, hydrogen yield and energy efficiency are doubled compared to the process using plasma alone or catalysis alone. Optical emission spectroscopic diagnostics technique has been employed to investigate the formation and the role of reactive radicals in the CH4/CO2 discharge. A chemical kinetic model has been developed to get a better understanding of the reaction mechanisms involved in the plasma-assisted hydrogen production process.
Investigation of biohydrogen production and uses from dairy cow slurry

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While global energy consumption steadily increases, the security of major fossil fuel reserves becomes more uncertain and irreversible damage is being done to the world's eco-systems to meet our energy demands. Hence the prospect of a hydrogen economy, to ensure our energy security, keep our ethical standards in place and protect the environment, is an appealing prospect for the future.

A potential hydrogen source is organic waste produced by agriculture, food and drinks industries. It is possible to produce a hydrogen-carbon dioxide gas mixture through biological treatment of this organic waste. I am interested in the impact utilising organic waste for hydrogen production can have on lowering green-house gas (GHG) emissions and replacing fossil fuel derived energy. Hydrogen generation from dairy cow slurry may offer the potential to treat waste and provide a renewable energy source. Currently, information describing the overall impact of using dairy cow slurry as source of renewable energy is limited. A life cycle analysis of the system provides information allowing conclusions to be drawn on the effectiveness of biohydrogen at substituting fossil fuel derived power, reducing GHG emissions and the economic viability.

Limited data is available on the separation of hydrogen and carbon dioxide gas mixtures. Polymer membranes offer the possibility of cheap and robust gas separation hence testing mixtures of hydrogen and carbon dioxide readily available membranes provides validating information for the LCA.
Photo-Electrochemical Production of Hydrogen with Solar Energy

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The incident solar power at the earth’s surface is ca. 125 000 TW, of which ca. 36 000 TW falls on land, whereas the global (thermal + electrical) power demand is ca. 15 TW. The feasibility of harvesting solar energy is well established technically and, increasingly so, economically, but its diurnal nature necessitates some form of storage. This can be achieved if electrons from photovoltaic panels are used e.g. to electrolyse water to form (oxygen and) hydrogen, which can be oxidised subsequently in fuel cells. Alternatively, solar energy can be used directly, and potentially more cheaply, for photo-electrochemical reduction (and oxidation) of water in an environmentally benign route to hydrogen (and oxygen). As in photovoltaic cells, a semiconducting material is used to absorb solar photons with energies greater than the semiconductor’s band gap, generating electrons in its conduction band (CB) and highly oxidising electron ‘holes’ in its valence band (VB) by reaction (1). The semiconductor needs to be chosen judiciously, so that electrons at its conduction band edge have sufficient energy (\(E_{CB} > E_{H_2O/H_2}\)) to reduce water to hydrogen by reaction (2), and holes at its valence band edge are sufficiently energetic (\(E_{VB} < E_{O_2/H_2O}\)) to oxidise water (or hydroxide ions at high pH) by reaction (3):

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\begin{align*}
\text{Semiconductor} + h\nu &\xrightarrow{\text{absorption}} \text{Semiconductor}(e_{CB}^-, h_{VB}^+) \\
2H_2O + 2e_{CB}^- &\longrightarrow H_2 + 2OH^- \\
2H_2O + 4h_{VB}^+ &\longrightarrow O_2 + 4H^+ \quad \text{or} \quad 4OH^- + 4h_{VB}^+ \longrightarrow O_2 + 2H_2O
\end{align*}
\]

Though the feasibility of such processes is well established, their deployment has been delayed by the lack of:

- Adequately stable semiconducting materials, well matched to the solar spectrum, to absorb light / photons with economically acceptable photon-to-hydrogen efficiencies;
- Semiconductors that produce hydrogen spontaneously without an electrical bias;
- Low cost electrocatalysts to enable such efficiencies to be achieved economically;
- Processes to produce acceptably efficient photo-electrodes at large scale and low cost;
- Suitable designs of reactors in which to deploy such materials.

Results will be presented for n-type hematite (\(\alpha-\text{Fe}_2\text{O}_3\)) spray-pyrolysed onto conducting fluorine-doped tin oxide (FTO) coated glass as photo-anode, connected electronically to a metallic cathode, at which hydrogen is evolved; oxygen evolution by reaction (3) is much slower than hydrogen evolution by reaction (2). A prototype 0.1×0.1 m² reactor, irradiated by a solar simulator, was designed, fabricated and is being characterised and modelled, to optimise its performance. The irradiance (W m⁻²) of the photo-anode produced a linear response in the photocurrent density (\(j\)) and hence in the specific hydrogen production rate, so a Fresnel lens was used to concentrate the photon flux. Hence, the means / geometries by which the photo-anode is illuminated and the spatial distribution of photon flux are important reactor design considerations, in addition to minimising the spatial distributions of electrical potential and current density.

Illuminating the \(\text{Fe}_2\text{O}_3\) photo-anode from the quartz window | electrolyte | \(\text{Fe}_2\text{O}_3\) | FTO glass side (front illumination) produced higher photocurrent densities than from quartz window | electrolyte | FTO glass | \(\text{Fe}_2\text{O}_3\) side (back illumination). A charge transport model was developed to predict reactor performance, explain experimental results and focus experimental work. This predicted that photocurrent densities are limited by transport of photo-generated minority charge carriers (holes), and that the back illumination would promote more charge recombination in the bulk by the reverse of reaction (1), so that less charge could be available to drive water splitting by reactions (2) and (3).
Simultaneously production of carbon nanotubes and hydrogen from glycerol reforming

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Abstract: The EU is the world leading region for biodiesel production with capacity of 9.57 million tonnes in 2010, by responding to climate change and energy security. One challenge for the further development of biodiesel is the large amount of by-product glycerol produced. Currently, steam reforming of glycerol for hydrogen production is attracting extensive attention, as hydrogen is regarded as an important energy carrier in future. In this work, we have used a novel method to simultaneously produce carbon nanotubes (CNTs) and hydrogen from glycerol reforming. Economic profits of the process could be enhanced significantly for the process, compared with traditional reforming process where hydrogen is the only product. In addition, producing useful carbons instead of CO₂ will also contribute to the carbon reduction target set by the world. Herein, we will report current updates in this topic in terms of increasing efficiency of production of CNTs and H₂, quality of CNTs, and the influence of catalyst. A nickel-based catalyst has been used. And also a stainless steel mesh has been investigated for producing CNTs and H₂, since it is low cost, and the separation of CNTs from stainless steel is simply.

Key Words: Carbon nanotubes, Hydrogen, Glycerol, Reforming
Increased Biohydrogen Production by Integrating Hydrogen Fermentation and Bioelectrolysis

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**Abstract**

The production of biohydrogen has been demonstrated from a wide range of lignocellulosic feedstocks which are not directly used for primary human food consumption. These substrates include wheatfeed (co-product of flour milling), whole crop maize, and fodder grass (*Lolium perenne*). The yields of hydrogen from these substrates is currently relatively low compared to the theoretical maximum, ranging from 7 to 64 m$^3$ H$_2$ per ton dry weight for wheat feed, 63 m$^3$ H$_2$ per ton dry weight for fodder maize and 76 m$^3$ H$_2$ per ton dry weight for wilted grass. Substantial energy remains either in the recalcitrant biomass or in the form of volatile fatty acids co-produced in the hydrogen fermentation process. These volatile fatty acids (principally acetate and butyrate) can be used in another bacterial catalysed process, microbial electrolysis to produce further hydrogen. By linking these two processes together the hydrogen yield from low grade lignocellulosic biomass could be increased from 2-3 mol H$_2$ mol$^{-1}$ hexose utilised to 7 mol H$_2$ mol$^{-1}$ hexose on substrate concentrations and loading rates which are commercially viable. These two processes will be linked by electrodialysis which should also increase the fermentative hydrogen yield by increasing substrate hydrolysis and reducing product inhibition.
Catalytic gasification of biomass for hydrogen production with in-situ CO\textsubscript{2} absorption using novel bi-functional Ni-Mg-Al-CaO catalyst

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Catalytic gasification of biomass in the presence of CaO is a promising route for CO\textsubscript{2} capture and thereby high yield hydrogen production. However, the non-stability of CaO sorbent for CO\textsubscript{2} absorption is a challenge for the process. A novel bi-functional Ni-Mg-Al-CaO catalyst has been prepared with different contents of CaO by integration of the catalytic and CO\textsubscript{2} absorbing materials to maximise hydrogen production. The prepared catalysts were tested for hydrogen production via the pyrolysis-gasification of wood biomass by using a two stage fixed-bed reaction system. Carbonation/calcination results using thermogravimetric analysis (TGA) in an atmosphere of N\textsubscript{2} or CO\textsubscript{2} showed that the reactivity of CaO with CO\textsubscript{2} decreased even after several cycles of carbonation/calcination, while the Ni-Mg-Al-CaO catalyst showed a comparative stable CO\textsubscript{2} absorption even after twenty cycles of carbonation/calcination. Adding CaO to the Ni-Mg-Al catalyst leads to an increase of hydrogen production and selectivity due to the enhancement of water gas shift reaction by in-situ CO\textsubscript{2} absorption. An optimal content of CaO was suggested to be 20 wt.% (weight ratio of CaO/Ni-Mg-Al) which produced the highest hydrogen production (20.2 mmol/g biomass) in the presence of Ni-Mg-Al-CaO catalyst. Temperature-programmed oxidation (TPO) showed that carbon deposition was significantly decreased with the addition of CaO in the Ni-Mg-Al catalyst, and with the increase of CaO content, coke deposition on the reacted catalyst was further decreased.
Optimal control strategies for hydrogen production when coupling solid oxide electrolysers with intermittent renewable energies

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Abstract

The penetration of intermittent renewable energies demands the development of energy storage technologies. High temperature electrolysis using solid oxide electrolyser cells (SOECs), as a potential energy storage technology, provides the prospect of a cost-effective and energy efficient route to clean hydrogen production.

This paper presents a study of optimal control strategies for hydrogen production based on SOEC technology, with the aim of offering efficient large-scale system operation when coupling an SOEC system with renewable energy sources. The system model used includes a 1D dynamic SOEC stack model and an air compressor model, to examine hydrogen production in relation to energy consumption. Control strategies considered include maximizing hydrogen production, minimizing SOEC energy consumption and minimizing compressor energy consumption. Optimal control trajectories of the operating variables over a given period of time show feasible control for the chosen situations. Temperature control of the SOEC stack is ensured via constraints on the overall temperature difference across the cell and the local temperature gradient within the SOEC stack, to link materials properties with system performance; these constraints are successfully managed. The relative merits of the optimal control strategies are revealed.