Plasma-assisted decomposition of gaseous propane to produce CO$_x$ free hydrogen

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Abstract
In this study, we survey the alternative approach of using plasma technology to produce CO$_x$ free hydrogen. In a corona discharge reactor operating at atmospheric pressure, electrons were energized by an electric field to ionize propane and induce chemical reactions. A range of each test parameter was covered, namely the effect of power input in the range of 4.5–105 W and discharge time of 1, 2, 3, 4, 5 and 8.18 min. A 19% hydrogen content by volume was achieved at a power input of 102 W and discharge time of 8.18 min.

Keywords: hydrogen economy; propane decomposition; CO$_2$ free hydrogen production; non-thermal plasma

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1 INTRODUCTION
Energy has played a major role in industrial development and economic growth throughout history. Energy extracted from fossil fuels such as coal, natural gas and crude oil has been the main drive of industrial growth since the nineteenth century. Concerns have arisen, as early as the 80s, for energy security as continuing economic growth in China, India and Brazil presents a higher global energy demand [1]; this cannot be sustained since oil reserves are finite and diminishing [2]. Dorian et al. [1] stated that if the world’s economy grows as expected, oil demand is projected to rise by 40 million barrels/day by 2030, and oil prices will continue to rise [1]. More recently, in 2003, the European ‘World Energy Technology and Climate Policy Outlook’ predicted an average growth rate of 1.8% per annum in 2000–30 for primary energy worldwide [3]. A similar growth rate of 1.5% per annum has been proposed by the International Energy Agency [4] for the period 2007–30, with an overall increase amounting to 40%. It has also been envisaged more speculatively that by 2050, global energy demand could double or triple and that the oil supply, of course, is unlikely to meet such a demand [5]. The oil crisis is clearly at an initial stage and is going to take dramatic dimensions. Overall, all forecasts point to the end of the great ‘oil era’ in the period 2030–40, with an accompanying severe increase in the cost of oil, leading to energy insecurity for many nations [6].

A further problem is that the widespread use of fossil fuels within the current infrastructure is now considered to be the largest source of anthropogenic emissions of carbon dioxide, which is a major contributor to the effects of global warming and climate change [7]. The OECD reported that in 1990 4 billion tons of CO$_2$ were released into the atmosphere from vehicle operations alone, with a figure of 8 billion tons forecasted for 2020 [6]. Ambitious targets set to reduce CO$_2$, however, can only be achieved through major efficiency and conservation gains [1].

Hence, global drivers for a sustainable energy future include: reducing global CO$_2$ emissions, ensuring the security of energy supply and creating a new industrial and technological base for energy [1]. The factors of finite fossil fuel resources and pollution both define the necessity of developing cleaner and more sustainable energy [8] and act as catalysts for an eventually revolutionary-like transition to a non-carbon-based global economy [1].

Alternative fuels must be technically feasible, economically competitive, environmentally acceptable and readily available. Fuels proposed and investigated for this purpose include biodiesel, methanol, ethanol, hydrogen, boron, natural gas, liquefied petroleum gas, Fisher–Tropsch fuel (such as synthetic diesel fuel), electricity (for use in batteries) and solar fuels (fuels generated using photovoltaic energy) [7]. Of these, hydrogen is the most attractive alternative to carbon-based fuels as it can be produced from diverse sources, namely: (i) renewable, including hydro, wind, solar and biomass, and (ii) non-renewable, including methane, coal and nuclear. Hydrogen can be utilized in high efficiency technologies, namely fuel cells for both vehicular transportation and distributed electricity generation [5]. Environmentally, its use avoids all of the major emissions [9].
'In a world where petroleum will become increasingly scarcer, hydrogen technology could significantly and quickly reduce energy system costs, improve greenhouse gas intensity, and help achieve sustainable economic development' [10]. Hydrogen and fuel cells are 'considered in many countries as an important alternative energy vector and a key technology for future sustainable energy systems in the stationary power, transportation, industrial and residential areas', as recognized by the Department of Energy (DOE) in 2004 and the European Commission [5]. A study commissioned by the UK Department of Trade and Industry found that hydrogen energy offers the prospect of meeting key UK policy goals for a sustainable energy future [5]. Hydrogen has been termed a 'wonder fuel' due to its superior characteristics including motivity, versatility, utilization efficiency, environmental compatibility, safety and economy. It has been argued that none of the other fuels such as petroleum, natural gas or syngas, approaches the performance levels of hydrogen when measured using the above criteria [11]. It is quite apparent that the majority of experts consider hydrogen technology to be a long-term solution for energy and environmental concerns [1, 2, 5–7]. Therefore, countries globally are developing road-maps to a future hydrogen economy and fuel cell deployment, and the global mentality as regards transition to a hydrogen economy is at the stage of when and how, not if [5].

Fuel cells are being developed for transportation as well as for stationary and portable power generation, with the aim of producing energy at improved efficiency, durability and lower emissions of gaseous contaminants such as CO, CO₂, NOx and SO₂. Stationary applications could vary from large central power stations to distributed-power generators for buildings, residences in urban areas and small systems located in remote areas. Fuel cell use for residential and distributed power generation systems may present some advantages over conventional energy generation systems (burning of fossil fuels in power stations), such as the reduction of transmission and distribution costs, improved quality of power delivery and the possibility of providing combined heat and electricity [12]. The use of fuel cells for domestic applications might be more acceptable to residential markets for on-site heat and electricity production, when compared with engine technologies which have moving parts, noise and vibration [13]. The use of fuel cells can also reduce carbon dioxide emissions by 49%, nitrogen oxide emissions by 91%, carbon monoxide emissions by 68% and volatile compound emissions by 93% when compared with traditional combustion technologies [14]. Proton exchange membrane fuel cells (PEMFCs) are an attractive type of fuel cells due to their reliability and robustness [15]. PEMFC is 'currently the one with the most advanced technological development and some cogenerative units are already commercialized' [16]. In the industry review 2011, Fuel Cell Today wrote that 'in terms of commercial success, the leader by far in terms of units shipments is the PEMFC' contributing 97.03% of shipments and 73.8% of MW supplied when compared with other fuel cell types in 2010 [17]. Commercialized PEMFC systems, which use a low-temperature PEM, have been reported to be able to give 1 kW electricity and 1.7 kW heat with a total efficiency of 85% [18]. Overall, the future of the hydrogen economy and fuel cell commercialization is highly dependent on the availability of low cost and environmentally friendly sources of hydrogen [19].

Up to the present day, hydrogen has been mainly produced from fossil fuels, through steam reforming of methane (SMR) or partial oxidation of hydrocarbon fuels [7]. SMR is the most popular route for hydrogen production from methane, contributing 48% of the world’s hydrogen production [7]. The SMR process generates a significant amount of atmospheric emissions of CO₂ which has a global warming potential of 13.7 kg/CO₂ equivalent per kilogram of the net hydrogen produced. For example, an SMR plant with a capacity of 1 million m³ hydrogen production generates 0.3–0.4 million m³ CO₂/day, which is normally vented to the atmosphere [20]. Pyrolysis of methane is a direct decomposition of methane into hydrogen and carbon black [21]. Dufour et al. [22, 23] have used a life cycle approach to compare conventional methods of hydrogen production from methane, namely steam reforming and pyrolysis. Their results show that even if carbon capture and storage technologies are used, the most environmentally friendly method is pyrolysis, avoiding the generation of CO₂ completely [23]. Hydrocarbon pyrolysis was also recognized as the most promising route for hydrogen production by Edwards et al. [5]. Abbas and Daud [9] concurred with Dufour et al. that the process is the best from the point of environmental pollution as it does not produce any CO₂. Pyrolysis is also a more economical option when compared with SMR with carbon capture [24]. The process co-produces valuable carbon products in solid form such as carbon black or graphite [25], this being much easier to sequester than carbon compounds in the gaseous form [9]. In the USA, ~5 million tons/year of carbon is used in the production of electrolytes for aluminum (requiring 0.4–0.5 kg per kg of aluminum) and by the ferroalloy industries. If the production of carbon were to increase, it could be used in other potential applications such as carbon to carbon composite use as building and construction material, electricity generation via carbon fuel cells and soil amendment [20]. However, in conventional technologies, pyrolysis of hydrocarbons is challenging from the catalyst stability point of view, as carbon deposition leads to catalyst deactivation.

Hydrogen production from gaseous hydrocarbons, such as propane, would especially benefit oil refineries where demand for hydrocarbon feedstock varies with time, so that the industry gains more flexibility in the feedstock choice [26]. Propane is attracting considerable attention in hydrogen production studies, primarily because it is a major constituent of liquefied petroleum gas [27]. In addition, propane is produced in relatively high amounts from natural gas and oil crude refining [28]. It is also attractive for on-board hydrogen generation, because of its being liquefiable and easy to store and transport [29]. Propane is an inexpensive fuel with a high energy density, and offers a new approach to more economical hydrogen production [30].
Based on the above rationale, our present work is focused on achieving decomposition of propane to generate CO\textsubscript{x} free hydrogen using the corona discharge non-thermal plasma method.

2 EXPERIMENTAL FACILITY AND METHODOLOGY

2.1 Design of the reforming unit

In order to investigate plasma-based pyrolysis of propane, the main apparatus is the corona discharge reforming unit itself. This is shown schematically in Figure 1a and b as a photograph of the plasma chamber with major components indicated.

The plasma chamber consists of two 316 stainless steel disks (23 mm thickness, 142 mm diameter), a stainless steel pin electrode, borosilicate glass cylinder, C103 copper disc with integrated cartridge heater (max output 500 W, 30 mm thickness, 142 mm diameter), PID temperature control system built in house, high-voltage power supply (Matsusada, max output \(\frac{30 \text{kV}}{5 \text{mA}}\)), vacuum pump (Edwards) and pressure gauge. The glass cylinder is 150 mm in length, 100 mm in outer diameter and 5 mm in thickness; it is made of borosilicate glass, which itself can sustain a maximum short-term working temperature of 500\(^\circ\)C and a maximum pressure of 73.7 bars. The top and bottom discs are connected and stabilized by three metal support rods. The working pressure in these experiments is quite low and of the order of 1–2 bar.

The bottom disc of stainless steel acts as a plate electrode. The chamber is designed to allow for tests with both liquids and gases, and in order to undertake tests involving liquid hydrocarbons, it has an integrated well to position a measured amount of liquid. The active electrode is installed at the center of the top disc and can be removed and changed to test different configurations. A glass rod serves as an insulator and for electrode stability purposes; it can be moved vertically to vary the inter-electrode distance. The outer end of the rod is connected to an extra high tension (EHT) lead at the inner end of the rod to provide the power supply for the active electrode. A positive direct current high voltage is applied to the active electrode from the HV generator through a 3.12 M\(\Omega\) resistor, creating a positive corona discharge.

2.2 Experimental method

The propane (referred to as working gas) is subjected to a positive corona discharge with argon, at atmospheric pressure and argon to propane ratio 1:1. In experiments with methane, it has been shown that argon addition enhances the rate of methane conversion to its radicals in plasma-assisted methane decomposition [31]. The amounts of propane and argon entering the system are measured by volume, using a pressure gauge. The chamber is first flushed with argon by exhausting to vacuum and then filling with argon (2 cycles) to ensure that there is no air in the system. Then the chamber is filled with 0.5 atmosphere argon and 0.5 atmosphere propane. High-voltage direct current power is supplied to the pin electrode, initiating electrical break down of the argon gas and hence generating active plasma species such as electrons and ions. Cracking of hydrocarbon molecules is achieved by plasma ionization of the hydrocarbon molecules by an impact of an energetic electron or photo-ionic decomposition (chemical reactions of ions induced by a photon) [32].

Gaseous samples are collected after each experiment and characterized by the GC-MS instrument comprising a Hewlet Packard series 5890 Gas Chromatography instrument and a Trio-1000 Mass Spectrometer. Gaseous products do not need any treatment and can be analyzed by the GC-MS directly. The products will also be tested by a GC to measure accurately the concentrations of hydrogen present.
3 RESULTS AND DISCUSSION

3.1 Effects of power input and discharge time on hydrogen production

A series of plasma decomposition tests were performed by varying the power input from 4.5 to 105.15 W, for each nominated discharge time of 1, 2, 3, 4 and 5 min. The inter-electrode distance and gas composition are kept constant at 15 mm and 1:1 argon to propane, respectively.

Figure 2 depicts the hydrogen production versus power input for different discharge times. The hydrogen production is defined as the percentage of the total volume after the experiment and measured by gas chromatography. As shown in Figure 2, at all discharge times tested, an increase in power input leads to a higher hydrogen generation, because the energy deposited on the feed gas (argon and propane in this case) increases with increasing power input. At discharge time 5 min, increasing power input from 4.2 to 102.65 W leads to an increase in hydrogen generation from 1.6 to 14.8% by volume.

Hydrogen production increases with increasing discharge time at all input power levels, as shown in Figure 2. A similar trend has been observed in the pulsed corona discharge reforming of methane [31]. However, as shown in the figure, there is a diminishing effect with discharge time, i.e. the increase from 4 to 5 min is small. This will be investigated further. The longer discharge time allows higher energy deposition on each molecule of the feed gas, resulting in higher conversion rates. At power inputs of just over 100 W, increasing the discharge time from 1 to 5 min, leads to an increase in hydrogen production from 8.33 to 14.88% by volume. A further increase to 8.18 mins (not shown in the figure) resulted in the hydrogen content of 19% at the power input of 102.65 W, not shown in the graph.

3.2 Decomposition mechanism and other compounds present

In methane conversion, energetic electrons collide with methane molecules and hence radicals H and CH₃ are formed, i.e. a pure plasma process. Mishra et al. [32] proposed a possible explanation for methane activation and conversion mechanisms under pyrolysis conditions in a pulse corona discharge [adapted Equations (1 and 4–8)]. This mechanism is adapted here for propane activation as follows:

\[
\text{CH}_4 + e^- \rightarrow \text{CH}_3 + H + e^- \quad (1)
\]

\[
\text{C}_3\text{H}_8 + e^- \rightarrow \text{C}_3\text{H}_7 + H + e^- \quad (2)
\]

The radical H may further react with another propane molecule to form an H₂ molecule and C₃H₇ radical:

\[
\text{C}_3\text{H}_8 + H \rightarrow \text{C}_3\text{H}_7 + \text{H}_2 \quad (3)
\]

With the addition of argon to the system, two extra processes may occur:

(1) Release of extra electrons:

\[
\text{Ar} \rightarrow \text{Ar}^+ + e^- \quad (4)
\]

(2) Production of excited Ar⁺ by reverse processes:

\[
\text{Ar} + e^- \rightarrow \text{Ar}^+ + e^- \quad (5)
\]

The latter accompanied by an emission of a photon, \(h\nu\):

\[
\text{Ar}^+ \rightarrow \text{Ar} + h\nu \quad (6)
\]

Or the direct capture of an electron by Ar⁺ and emission of a photon:

\[
\text{Ar}^+ + e^- \rightarrow \text{Ar}^- + h\nu \quad (7)
\]

Reaction (4) provides extra electrons for propane activation by an energetic electron, the process described in Equation (2), i.e. a chemical reaction initiated via the collision with an electron, which is not consumed by the reaction. Reaction (7) generates photons assisting in photo-ionic decomposition of propane. A full decomposition of propane would result in the generation of pure carbon in the solid state and pure hydrogen in a gaseous state:

\[
\text{C}_3\text{H}_8 \rightarrow 3\text{C} + 4\text{H}_2 \quad (8)
\]

Table 1 shows the list of compounds, other than hydrogen, generated (recorded by the GC-MS) during corona discharge decomposition of propane. Production of methane, ethene and ethane can be explained by an incomplete propane decomposition and hence the generation of smaller molecules. However, from Table 1, it can also be seen that larger molecules than the original have been generated.
The recombination of these radicals would result in the formation of benzene:

\[ C_3H_3 + C_3H_3^+ \rightarrow C_6H_6 \]  

(10)

4 CONCLUSIONS

In this study, we have presented a short review of the importance of hydrogen and the significance of the ability to reduce CO₂ emissions during its production. Propane has been identified as a potentially useful feedstock.

The survey forms the background to reporting the development of a non-thermal plasma reforming unit operating at atmospheric pressure for converting gaseous hydrocarbons to CO₂ free hydrogen. A series of experiments has been performed to investigate the effects of power input and discharge time on hydrogen production by plasma decomposition of propane. We have shown that higher power inputs and longer discharge time favor the production of hydrogen. A hydrogen concentration by volume of nearly 20% has been achieved at a power input of 102 W, discharge time 8.18 min, inter-electrode distance 15 mm and argon to propane ratio 1:1.

The ongoing work includes further parametric studies of the effects of inter-electrode distance, gas composition and the polarity of corona discharge on hydrogen generation.

REFERENCES


