Non-Thermal Plasma Reactor for Decomposition of Propane to Generate CO$_x$ Free Hydrogen

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Abstract—Non-thermal plasma reforming unit operating at atmospheric pressure has been developed for converting propane to CO$_x$ free hydrogen. Argon was used to provide additional electrons and photons for higher reaction rates. A series of experiments have been performed for positive corona discharge at 15 mm inter-electrode distance to study the effects discharge power and residence time. A range of each test parameter was covered, namely, the effect of discharge power in the range of 19 – 35 W and residence time of 60 to 303 seconds. The results analysis shows that both, the discharge power and the residence time, have a positive influence on propane conversion, hydrogen selectivity and energy conversion efficiency. Propane conversion and hydrogen selectivity are both highest at the largest discharge power of 35 W and the longest residence time of 303 s.

Index Terms—CO$_2$ free hydrogen production, non-thermal plasma, propane decomposition.

I. INTRODUCTION

Limitations of fossil fuel resources and concerns about climate changes associated with global warming led to the first World Hydrogen conference in 1976, which identified hydrogen as a clean energy carrier for the future [1]. Present hydrogen is produced almost exclusively through steam methane reforming (SMR), generating a significant amount of atmospheric CO$_2$ emissions [2], [3]. Hydrocarbon pyrolysis is an alternative method of hydrogen generation, it involves a direct decomposition of gaseous hydrocarbons into hydrogen and carbon black [4]. Pyrolysis is the most promising alternative for producing hydrogen from hydrocarbons [5]. The process is most environmentally friendly as it does not produce any CO$_2$ [3] and is more economical than SMR with carbon capture [6]. In search for alternative sources of hydrogen, propane is attracting considerable attention in hydrogen production studies as it is a major constituent of LPG, produced in relative amounts in oil refining processes [7], is easily stored and transported [8], [9] and is inexpensive [10]. For steam reforming of propane, industrial operations use excess of steam to minimize catalyst deactivation by carbon deposition. However, excess steam results in reduced hydrogen yields and higher CO$_2$ emissions [11]. Nickel based catalysts are preferred for steam reforming due to its activity and the low cost [11]. The use of precious metal catalysts such as ruthenium for steam propane reforming [12], [13] and auto thermal reforming [14], and rhodium for partial oxidation [15] and steam reforming [16] can achieve nearly 100 % propane conversion and impressive hydrogen selectivities. However, the use of high temperatures and precious metals are not favourable from the cost and feasibility point of view. Also, all of the catalytic systems above generate CO$_x$ compounds due to the addiction of oxygen species in the system because the catalysts cannot tolerate carbon deposition.

Decomposition or pyrolysis method to produce hydrogen is the most attractive from the environmental point of view as described above. However, this reaction is challenging from catalyst stability point of view due to the deposition of solid carbon causing deactivation of the catalyst [11]. Decomposition of propane using catalysts such as nickel and bi-metallic nickel-copper [17], iron and bimetallic iron-palladium, iron-molybdenum and iron-nickel [18], activated carbon based metal catalysts (TM-AC), where TM is manganese, iron, cobalt, vanadium or nickel [19] have been reported in the literature. Solovyev et al. [17] performed experiments for non-catalytic propane pyrolysis, and nickel and nickel-copper catalytic propane decomposition for CO$_x$ free hydrogen and carbon nanofiber generation. Pyrolysis experiments at 700 °C resulted to almost 90 % propane conversion, but only 11 % hydrogen content was achieved, with main product being methane. The authors believe this is mainly due to dominating of C-C bond breaking rather than higher energy C-H bond. In the experiments with nickel catalyst, 95 % of propane conversion was achieved with the only gaseous products being 35 % hydrogen and 65 % methane, at 550 °C in the first 1.5 hour of the reaction [17]. However, as the processing exceeds 1.5 hours, propane conversion and reactant concentrations decreased until nearly no effect observed at 4 hours due to catalyst deactivation. The addition of copper to nickel to generate bi-metallic catalyst has increased the lifetime of the catalyst and hydrogen selectivity. When 50 % nickel – 40 % copper bi-metallic catalyst was used at 600 °C, highest propane conversion and hydrogen concentration was at the first hour of operation, equalling to 80 and 60 % respectively. As the time on stream increased, propane conversion gradually decreased together with hydrogen concentration in the stream equalling to 35 and 25 % respectively after 12 hours of operation. Further decrease is noted by the authors as the operation time reaches 45 hours [17]. Even though the propane decomposition system proposed by Solovyev et al. [17] yields pure and CO$_2$ free hydrogen and valuable carbon nanofibres, the main problem of catalyst deactivation in the case of nickel, or partial deactivation in the case of nickel-copper still remains. This could be a major issue if the process was to be adapted for industrial or commercial hydrogen generation applications. Wang et al. [18] have also reported

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experimental results for non-catalytic propane pyrolysis, as well as catalytic decomposition employing iron catalyst and bimetallic catalysts iron-palladium, iron-molybdenum and iron-nickel for CO$_2$ free hydrogen and solid carbon generation. Under non-catalytic pyrolysis conditions of 750 °C the group reported a high propane conversion of 100 %. The gaseous products were 45 % methane, 25 % hydrogen and 15 % acetylene [20]. Similarly to Solovyev et al. [17], Wang et al. [18] concluded that C-C bond breakage dominates under the pyrolysis conditions of propane. For all catalysts employed by Wang et al. [18], methane selectivity dominated the process at temperatures of 450 – 500 °C. Highest hydrogen generation of just over 80 % by volume was achieved at 625°C by employing bi-metallic catalysts nickel-iron and molybdenum-iron in the first 30 minutes of operation. Hydrogen concentration only decreased slightly to approximately 60 % after prolonged operation of 6 hours. For both iron and palladium-iron catalysts, hydrogen generation decreased sharply after only 2 hours of operation. Hence, as in the case of nickel-copper catalyst employed by Solovyev et al. [17], carbon deposition and catalyst deactivation problems occurred in the catalytic systems proposed by Wang et al. [18] and could be a major culprit. Solovyev et al. [17] reported 50% hydrogen concentration for nickel-copper catalyst after 6 hours of operation. Hence, nickel-iron and molybdenum-iron catalysts show only slightly better carbon deposition resistance than nickel-copper catalyst. The results for nickel-iron and molybdenum-iron were only reported for 6 hour operation showing a gradual hydrogen concentration decrease [18]. Longer than 6 hour time-on-stream might give more insight to the effects of prolonged operation on hydrogen generation and catalyst resistance to carbon deposition.

Reasonable propane conversions and hydrogen selectivities were achieved for catalytic propane decomposition systems. However, time on stream experiments revealed that carbon deposition and catalyst deactivation problems occurred, drastically reducing propane conversion ability and hydrogen selectivity. Non-catalytic pyrolysis of propane has been achieved at high temperatures above 700 °C with high propane conversion of above 90 %. However, the main product generated was methane, with very low yields of hydrogen [17], [18].

Application of plasma technology in the production of hydrogen can eliminate or decrease problems associated with catalyst sensitivity and deterioration [4]. Non-thermal plasmas especially are considered to very promising for organic synthesis applications. However, the present understanding of plasma chemistry is limited and most of the present achievements are based on experimental data [21]. Non-thermal plasmas have been successfully applied to hydrogen production from methane, liquid hydrocarbons and biomass. Non-thermal plasmas including atmospheric pressure microwave discharges [22] and pulsed plasma discharges [23]-[26] have been successfully applied for direct methane decomposition to hydrogen and carbon. Corona discharge is non-thermal plasma formed on sharp points, edges or thin wires where the electric field is sufficiently large [27]. Corona discharges have been used in a wide range of applications including the production of hydrogen from methane [26], [28]-[30].

Based on the above rationale, our present work is focused on achieving decomposition of propane to generate CO$_2$ free hydrogen using the corona discharge non-thermal plasma method.

II. EXPERIMENTAL FACILITY AND METHODOLOGY

A. Design of the Reforming Unit

The experimental set-up consists of a plasma reactor, high voltage power supply (Matsusada, max output = 30 kV, 5 mA), vacuum pump (Edwards) and temperature and pressure data logging system (PiccoLog), and has been described in more detail in [30]. The chamber contains gaseous product outlet septa and dry carbon powder is collected directly from the plate electrode. The pin serves as an active electrode and is supplied with either positive or negative high voltage generating either positive or negative corona discharge respectively. High voltages are only necessary for the plasma ignition, after the ignition plasma can sustain itself at much lower voltages. Therefore, during the experiments high positive voltage is applied to the active electrode from a HV generator through a 3.14 MΩ in house built resistor (measured with 0.05 % accuracy). The resistor allows the plasma ignition and sustainability by lowering the voltage input after the ignition. The discharge power $P_D$ in watts is the actual power between the pin and the plate electrodes, not including the losses due to the power supply arrangement, and is calculated using the formula:

$$P_D = I(V - IR)$$

where $I$ is the current in amps, $V$ is the voltage in volts and $R$ is the resistance in ohms.

B. Experimental and Analytical Method

Propane is subjected to a positive corona discharge with argon, total volume of 1 atmosphere and ratio 1:1 in a batch process. Partial pressures are used for measuring propane and argon entering the system [31], using a pressure transducer connected to the data logger. 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.

The Gas chromatography mass spectrometer (GC-MS) used in this study is comprised of Hewlet Packard series 5890 Gas Chromatography instrument and a Trio-1000 Mass Spectrometer, and is calibrated to measure propane in the range of 30 – 50 % with the accuracy of ± 2.08 % of the reading value. Each sample is analysed by the GC-MS after the plasma unit is filled with propane and argon mixture (before the plasma experiment) to determine accurate concentration of input propane, and after each experiment to determine the amount of propane un-reacted and any other compounds present. GC-MS instrumentation is very sensitive and is able to determine all of the gaseous compounds present in the sample. The instrumentation has not been calibrated for all of the compounds generated via propane decomposition, as it is not possible to have such a specific calibration mixture of these compounds. Therefore, for comparison reasons, the
values extracted are in arbitrary units, i.e. the measured areas of the peaks on the chromatograms. Arbitrary units do not give enough information to quantify the compounds, but they can be used for comparison of compound behaviour and appearance between the samples and the sets. After each experiment samples are also tested for accurate hydrogen measurement, using the Chromopack CP9001 GC set up specifically for hydrogen analysis. The GC is calibrated to measure hydrogen in the range of 0 – 30 % with the accuracy of ± 2.06 % of the reading value.

C. Reaction Performance Evaluation

Product selectivity, conversion rate of the reactants and the efficiency of the system are three main factors used to determine viability of the process to produce hydrogen or syngas from hydrocarbons. The formula for propane conversion in percent is presented below and is well used and accepted in literature [32]:

\[
X_{C_3H_8} (%) = \frac{n_{in} - n_{out}}{n_{in}} \times 100 \tag{2}
\]

where \( n \) denotes the amount of compound in moles in or out, \( n_{in} \) and \( n_{out} \) respectively. The selectivity towards hydrogen for propane is calculated as follows [20]:

\[
S_{H_2} (%) = \frac{2}{6} \times \frac{n_{H_2}}{convC_2H_4} \times 100 \tag{3}
\]

where \( n_{H_2} \) and \( convC_2H_4 \) are the moles of hydrogen generated and propane converted respectively.

The energy conversion efficiency (ECE) is calculated using the higher heating values (HHV) of propane (50, 350 kJ/kg) and hydrogen (141,800 kJ/kg) and the electric power consumed (\( P_d \)) in kilowatts, hydrogen production \( pH_2 \) and propane consumption \( cC_2H_8 \) being in kilograms (adapted from [20]):

\[
ECE = \frac{pH_2 \times HHV_{H_2}}{P + cC_2H_8 \times HHV_{C_2H_8}} \tag{4}
\]

III. RESULTS AND DISCUSSION

A. Propane Conversion

Higher discharge powers and higher residence time both lead to higher propane conversion, as shown in Fig. 1a. The energy deposited on propane molecules increases with increasing discharge power and residence time. This is shown in Fig. 1b, where propane conversion is compared to the total discharge power into the system.

B. Hydrogen Generation and Selectivity

Hydrogen production increases with discharge power and time, and with total discharge power, see Fig. 2. The energy deposited on the feed gas increases with increasing the discharge power, where higher residence time allows higher energy deposition on each molecule of the feed gas, both resulting in higher conversion rates and hence an increase in hydrogen production.

Hydrogen selectivity is a very important measure of energy conversion performance as it shows the percentage of propane being converted into the desired fuel hydrogen. Fig. 3a shows that hydrogen selectivity increases with both, the discharge power and the residence time. However, there is a diminishing effect on hydrogen selectivity with discharge power at residence times above 2 minutes, see Fig. 3a, Fig. 3b shows that hydrogen selectivity also increases with the total discharge power. However, it can also be seen that there is a diminishing effect with total discharge power, i.e. the increase from 7 to 10 kJ is very small (0.16 %), even though as seen in Fig. 2, hydrogen generation increases nearly linearly with discharge power. The diminishing effect in hydrogen selectivity can be explained by looking at the generation of other compounds in the system. The decomposition mechanism and a clear list of compounds generated of propane under a positive corona discharge have been described in [1]. Generation of ethane, 2, 5 – cyclohexane, 1-propyne and 1-buten-3-yne increased with total discharge power. The generation of all compounds were found to be favoured by higher discharge powers, which explains the diminishing hydrogen selectivity with increased residence time.
C. Energy Conversion Efficiency

Energy conversion efficiency for the system determines how efficiently propane energy and electric energy is converted to the desired fuel hydrogen. From Fig. 4a it can be seen that energy efficiency increases with discharge power. Increasing the residence time from 1 to 2 minutes has a very high positive effect on the efficiency at approximately 23 W, a diminishing effect is seen as the discharge power is further increased at 2 minutes residence time. Fig. 4b shows that a diminishing effect occurs at total discharge power above 4 kJ. From Fig. 5, it can be clearly seen that energy conversion efficiency increases nearly proportionally with hydrogen selectivity. Due to the very low energy input in the form of electricity and high calorific value of hydrogen, the energy conversion efficiency is mainly governed by hydrogen selectivity.

![Graph showing energy conversion efficiency against discharge power and residence time.](image)

Fig. 5. The relationship between hydrogen selectivity and energy efficiency. The combined total error is ± 5.5% of the reading value. Constant conditions: inter-electrode distance 15 mm, propane to argon ratio 1.

IV. CONCLUSIONS

In this paper 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 with decomposition being the most favourable method of hydrogen generation.

The survey forms the background to reporting the development of a non-catalytic 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 discharge power and residence time on propane conversion ability, hydrogen production and energy conversion efficiency by plasma decomposition of propane. We have shown that higher discharge powers and longer residence time favours the conversion of propane and production of hydrogen. Hydrogen selectivity is highly affected by other compound generation, which also increase with discharge power and residence time. Energy conversion efficiency is mainly governed by hydrogen selectivity, due to its high calorific value. For corona discharge at 15 mm inter electrode distance, 48% propane conversion with 33% hydrogen selectivity and 11% energy conversion efficiency have been achieved at 35 W discharge power and 303 s residence time.

Ongoing work includes further parametric studies of the effects of inter-electrode distance, gas composition and the polarity of corona discharge on hydrogen generation. One of
the key challenges is increasing hydrogen selectivity and hence, energy conversion efficiency within the system.

**REFERENCES**


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