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Experimental Study of Electric and Spectroscopic Characteristics of Electric Discharge in LPG

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Abstract

Electric discharge has been carried out in LPG using DC high voltage (0.4 - 3 KV) at gas pressure in the range of 1 to 25 torr. The electric and spectroscopic characteristics of the discharge were studied at different discharge conditions. Deviations from Paschen's law were observed as a result of the change of the distance between the two the electrodes. Two discharge modes, namely glow discharge and spark discharge modes, has been observed in the discharge current waveforms. The discharge current waveforms indicate a repetitive pulsed behaviour with frequencies of 5 kHz to 5 MHz depending upon the applied voltage and the gas pressure. The emitted spectra from the discharge are also studied near both the cathode and the anode using different electrode materials. H_α line and C2 Swan band system are observed, which confirms the conversion of LPG to hydrogen and carbon clusters.

1. Introduction

Liquefied petroleum gas (LPG) is a mixture of hydrocarbon-based gases, mainly propane and butane gases. Natural gas purification produces about 55 percent of all LPG, while crude oil refining produces about 45 per-

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cent. LPG is widely used as a household fuel for heating and cooking in many countries. Its transportability and easy storage have boosted its popularity. LPG is rarely used as a vehicles fuel although it generates lower air pollutants than gasoline [1] even though lower energy output, (about 74% of the gasoline energy output) is expected [2]. The low energy output of LPG reduces the interest of using it as a common alternative fuel for vehicles. To overcome the low energy output some reforming of LPG is required.

Recently electric discharge has been widely used for reforming the hydrocarbon gases. Although there are some publications in the literature for using the electric discharge for the conversion of methane, ethane, acetylene and other hydrocarbons to hydrogen [3]-[6], there is shortage in the investigations of the conversion of LPG to hydrogen using the electric discharge technique in the literatures. The electric discharge is expected to be an efficient technique for conversion of LPG to other alternative fuel gases such as hydrogen. Investigation of the electric and spectroscopic characteristics of the electric discharge in LPG is one of the important keys to understand the conversion mechanisms and achieve efficient reforming of LPG.

The aim of the present work is to explore the discharge mechanism in LPG by studying the electric and spectroscopic characteristics of the discharge.

2. Experimental Setup

Figure 1(a) shows a schematic diagram of the experimental setup of the electric discharge system. **Figure 1(b)**
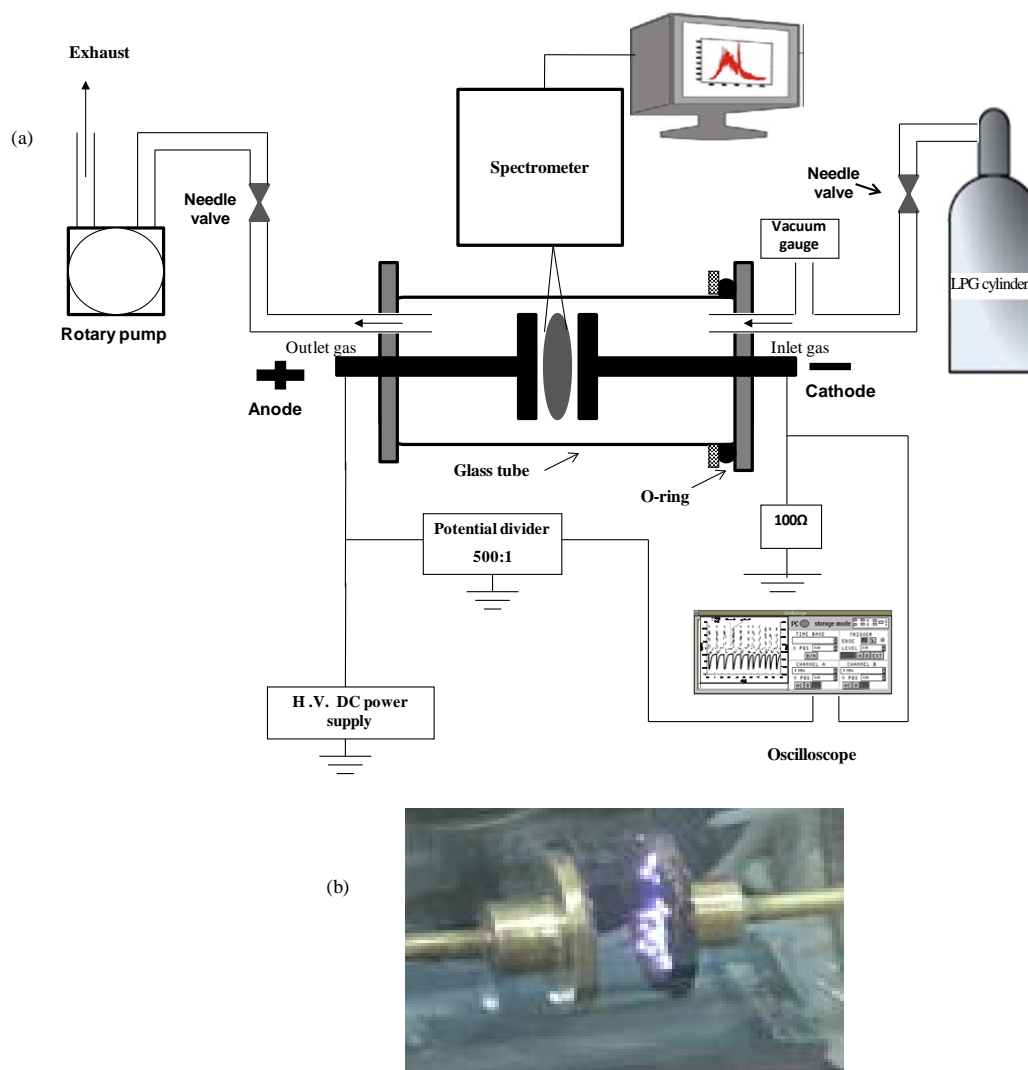

Figure 1. (a) Schematic diagram of the experimental arrangements; (b) photographic plate of the LPG discharge.

shows a photographic plate of the discharge in LPG. The discharge cell consists of a cylindrical glass vessel with 80 mm diameter and 110 mm length. Two movable electrodes have been placed on the axe of the glass tube. The electrodes are made of brass (alloy of copper and zinc) and they are coated with nickel in some measurements. The electrode diameter is 30 mm, and the gap distance between the two electrodes is varied from 1 to 10 mm. The vessel has been evacuated to base pressure of 10^{-2} torr using rotary pump and then the LPG has been left to flow through the discharge cell at constant flow rate of 1 L/min. The used samples of LPG consist of about 65% butane (C_4H_{10}) and 35% propane (C_3H_8). Some traces of other hydrocarbons such as ethane, ethylene, propylene, butylene, etc are also expected. Using two needle valves, before and after the vessel, the LPG pressure in the vessel has been controlled in the range of 1 - 25 torr. A DC power supply (0 - 3 kV) has been used as high voltage source. A resistance of 22 kΩ has been used to limit the discharge current. The discharge voltage has been measured via a potential divider (500:1) while the discharge current has been measured by measuring the potential drop across a resistance of 100 Ω. The voltage and current waveforms have been recorded using digital storage oscilloscope (type HM1508). A spectrometer (Type: Solar laser systems M266) has been used for the spectroscopic measurements. The slit width of the spectrometer has been adjusted to be 50 microns.

3. Results and Discussion

3.1. Electric Characteristics

The breakdown voltage (V_b) of LPG has been measured at different values of gas pressures and distances between the two electrodes. **Figure 2** shows the Paschen's curve at a distance of 1 mm between the two electrodes and different values of the gas pressure *i.e.* different pd. The minimum breakdown voltage (V_{bmin}) has been found to be 0.47 kV at pd value of 0.42 torr.cm (pd_{min}). **Figure 3** shows the Paschen's curves at different distances between the two electrodes. A deviation from Paschen's curves has been noticed as shown in **Figure 3**, where the values of V_b at the same Pd do not coincide. Higher breakdown voltages have been obtained at longer distances between the two electrodes and at the same values of pd. A similar deviation has been reported in the literatures for the inert gases (e.g. helium, neon, argon, krypton, and xenon) [7]-[9]. No deviations from Paschen's law for hydrocarbon gases were reported in the literatures. The deviation from Paschen's law occurs when the active secondary ionization processes at the electrodes surface or in the discharge volume are due to the photons and/or the excited atoms or molecules [8]. This confirms the importance role of the photons and/or the excited atoms and/or molecules as a secondary ionization processes in the electric breakdown of LPG in the present discharge conditions.

Figure 4 shows the discharge voltage and the discharge current waveforms in LPG at a gas pressure of 20 torr and 3 mm distance between the two electrodes. Two different components of the discharge current are observed in **Figure 4**, a glow discharge mode and a spark discharge mode. The glow discharge component mode is characterized by a uniform current of low values in the order of few tens of mA, while the spark discharge component is characterized by high current component in the order of hundreds of mA with a pulsed behaviour of a very short time (around 50 ns). The photographic plate in **Figure 1(b)** indicates that the discharge in LPG is very bright discharge channels that are rotating upon the electrode surface. The spark channels play an important role in the conversion processes of the hydrocarbons to hydrogen.
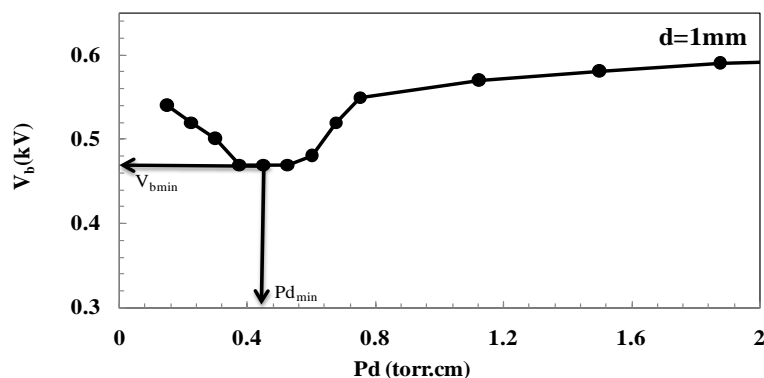

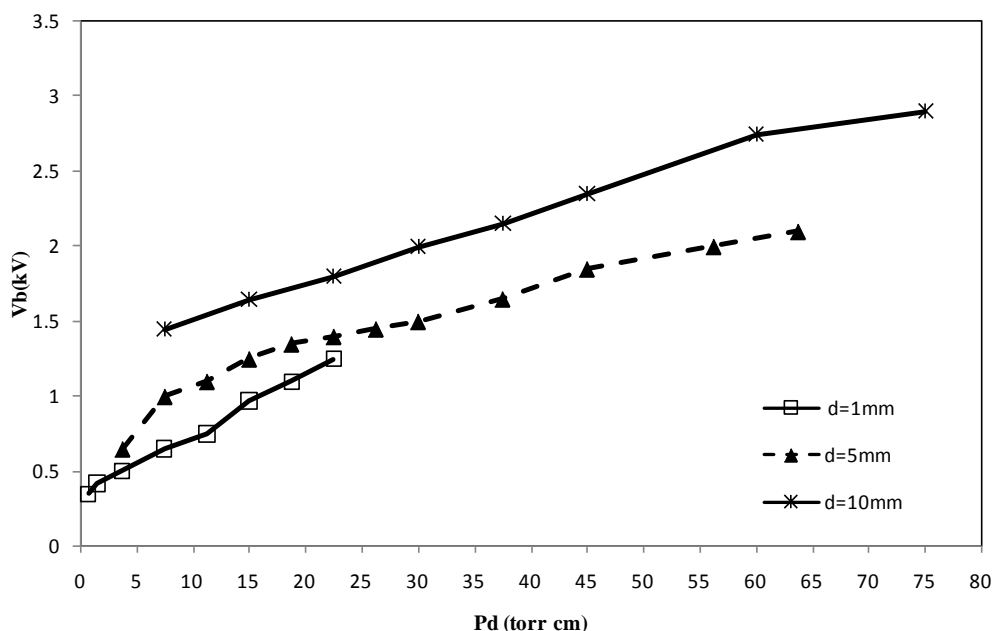**Figure 2.** Paschen's curve at 1 mm distance between the two electrodes.

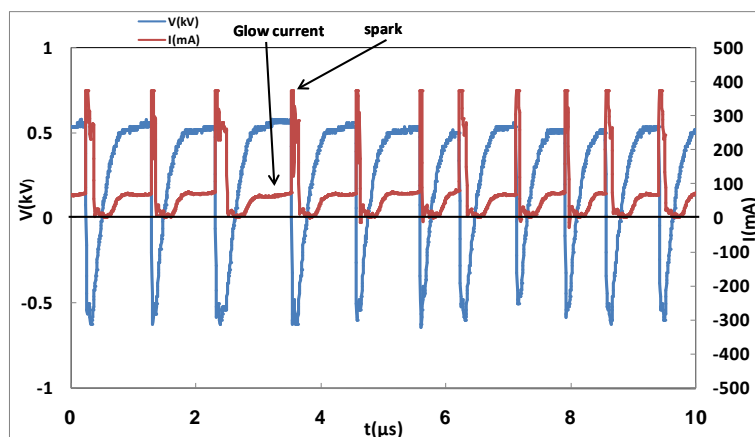**Figure 3.** Paschen's curves at different distances between the two electrodes.
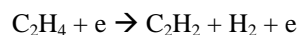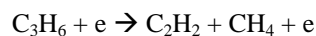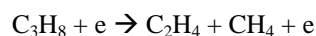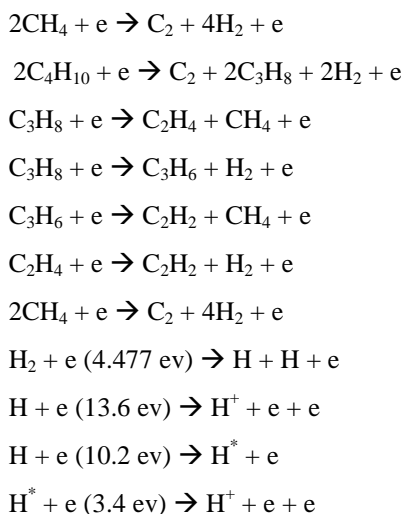

Figure 4. Voltage and current waveforms.

The transition from glow to spark discharge modes can be explained as follows: as the glow discharge mode is formed some of propane and butane molecules are decomposed forming hydrogen atoms and different carbon species. The hydrogen atoms play an important role in increasing the ionization processes in the gas and hence transforming the discharge mode to spark mode and subsequently increases the current very sharply to very high value [10] [11]. The enhancement of discharge current as a subsequent increase in the produced H atoms is related to the increase of the ionization processes through:

Ionization of H atoms and through the following processes:

1) The secondary ionization process produced by the hydrogen metastable state H[*] which has a relatively long lifetime up to o12 sec [11]. According to the following reactions [11]-[15]:

$$C_3H_8 + e \rightarrow C_2H_4 + CH_4 + e$$

$$C_3H_8 + e \rightarrow C_3H_6 + H_2 + e$$

$$C_3H_6 + e \rightarrow C_2H_2 + CH_4 + e$$

$$C_2H_4 + e \rightarrow C_2H_2 + H_2 + e$$

$$2CH_4 + e \rightarrow C_2 + 4H_2 + e$$

$$2C_4H_{10} + e \rightarrow C_2 + 2C_3H_8 + 2H_2 + e$$

$$C_3H_8 + e \rightarrow C_2H_4 + CH_4 + e$$

$$C_3H_8 + e \rightarrow C_3H_6 + H_2 + e$$

$$C_3H_6 + e \rightarrow C_2H_2 + CH_4 + e$$

$$C_2H_4 + e \rightarrow C_2H_2 + H_2 + e$$

$$2CH_4 + e \rightarrow C_2 + 4H_2 + e$$

$$H_2 + e \, (4.477 \text{ ev}) \rightarrow H + H + e$$

$$H + e \, (13.6 \text{ ev}) \rightarrow H^+ + e + e$$

$$H + e \, (10.2 \text{ ev}) \rightarrow H^* + e$$

$$H^* + e \, (3.4 \text{ ev}) \rightarrow H^+ + e + e$$

An increase in the concentration of the H and subsequently H^* atoms lead to increase in the secondary ionization processes and hence will lead to an increase in the discharge current which will lead to the transformation of the glow mode to spark mode discharge.

2) Also the gas temperature will be elevated and therefore the density of the gas in the discharge volume will decrease and this will in turn increase the reduced electric field (E/N) in the gas and consequently share in increasing the spark discharge current enhancement.

Also the fast increase in the current of spark discharge mode to hundreds of milliamperes in nanoseconds can lead to:

1) Back electromotive force can be generated where its magnitude is proportional to the ratio—*dI/dt*.

2) The gas temperature elevation will in turn increases the reduced electric field (E/N) in the gas and consequently enhance the spark discharge current.

3) High density sheaths of charged particles are generated in the discharge volume.

Accordingly, due to the above factors a sharp drop in the discharge voltage will take place (see **Figure 4**) As the voltage is dropped, the discharge current cannot be sustained anymore and hence the discharge is collapsed and consequently a sudden drop in the discharge current can be noticed in **Figure 4**. Following the discharge collapses, the sheaths disappear due to the deionization processes then the voltage recovers again to its applied value and hence new cycles of the discharge process are repeated. This mechanism of the discharge gives the discharge its repetitive pulsed behaviour which is shown in **Figure 4**.

As can be seen in **Figure 4**, the voltage not only drops to its applied value but also decreases more till it reaches negative values. This behaviour is not only because of the formed sheaths but also because of the back electromotive force generated in the circuit. While the spark discharge is formed, the current increases at a very high rate (*dI/dt*) which is about 2×10^7 A/s. This very high rate of *dI/dt* forms a back electromotive force which causes the reverse negative voltage in the discharge circuit.

Figure 5 shows the average estimated repetition frequency f as a function of the applied voltage at gas pressure of 5 torr and gap distance of 3 mm. It can be seen that, as the discharge voltage increases the repetition frequency increases. This can be attributed to the increase in the reduced electric field which in turn accelerates the ionization processes and hence reduces the time required for one complete discharge cycle to take place. The results in **Figure 4**, indicate that the repetition frequency of the discharge can be controlled in the range (0.1 - 2 MHz) using applied voltage in the range of (0.6 - 2 kV). The repetition frequency can be controlled also by gas pressure. At applied voltage of 0.6 kV, the repetition frequency has been decreased from 100 kHz to 5 kHz, as the gas pressure increases from 5 torr to 25 torr. In the present work conditions the repetition frequency can be controlled in a wide range from 5 kHz up to 5 MHz.

3.2. Spectroscopic Characteristics

Figures 6-9 show light spectra emitted from LPG discharge near the cathode and near the anode surfaces (electrodes were made of Brass and Nickel). Various lines and bands can be recognized in these figures.
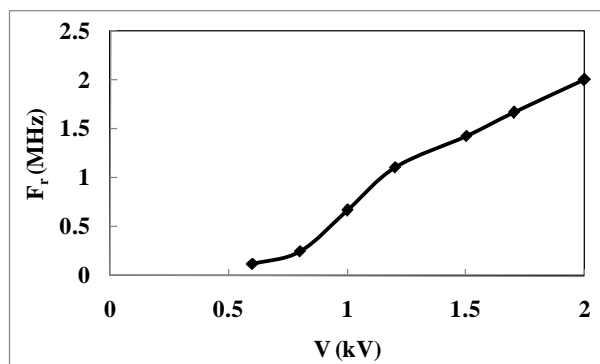
Figure 5. The repetition frequency of the discharge as a function of the applied voltage.
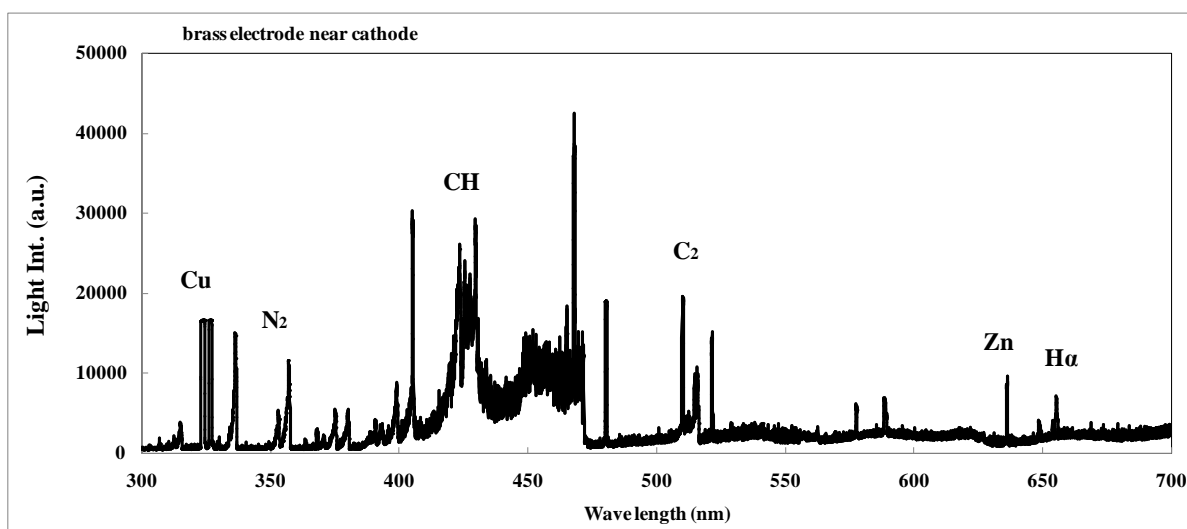

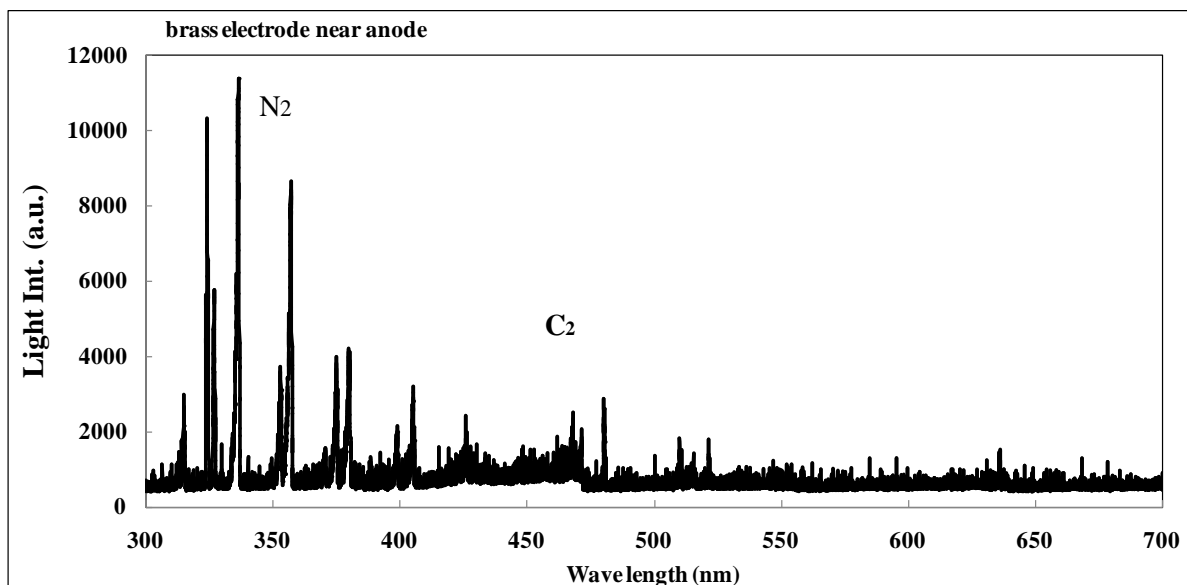**Figure 6.** Light spectrum emitted from LPG discharge near the cathode using brass electrodes.

Figure 7. Light spectrum emitted from LPG discharge near the anode using brass electrodes.
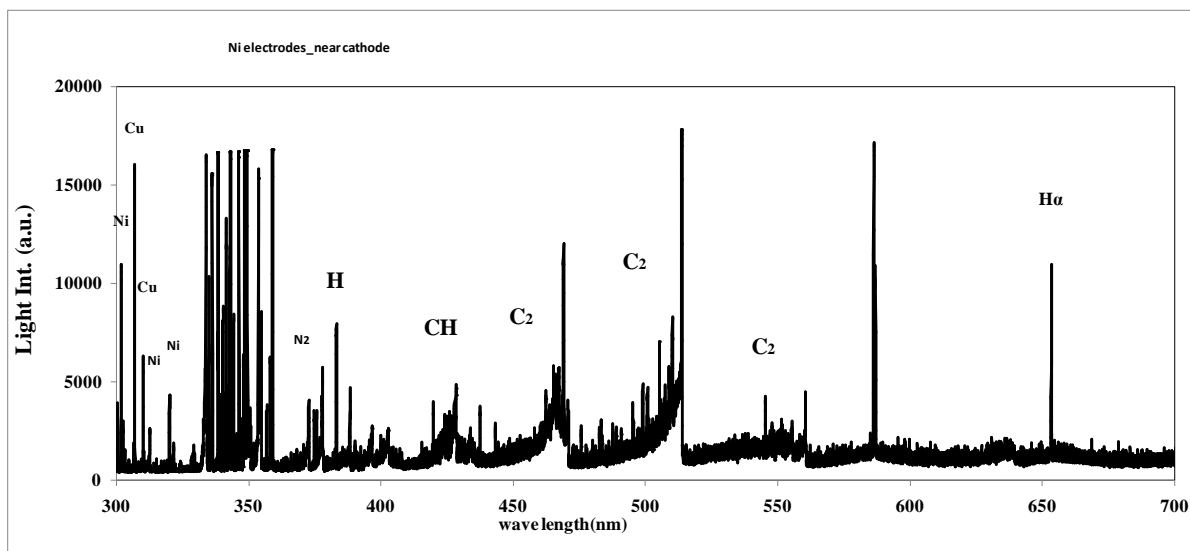
Figure 8. Light spectrum emitted from LPG discharge near the cathode using Ni electrodes.
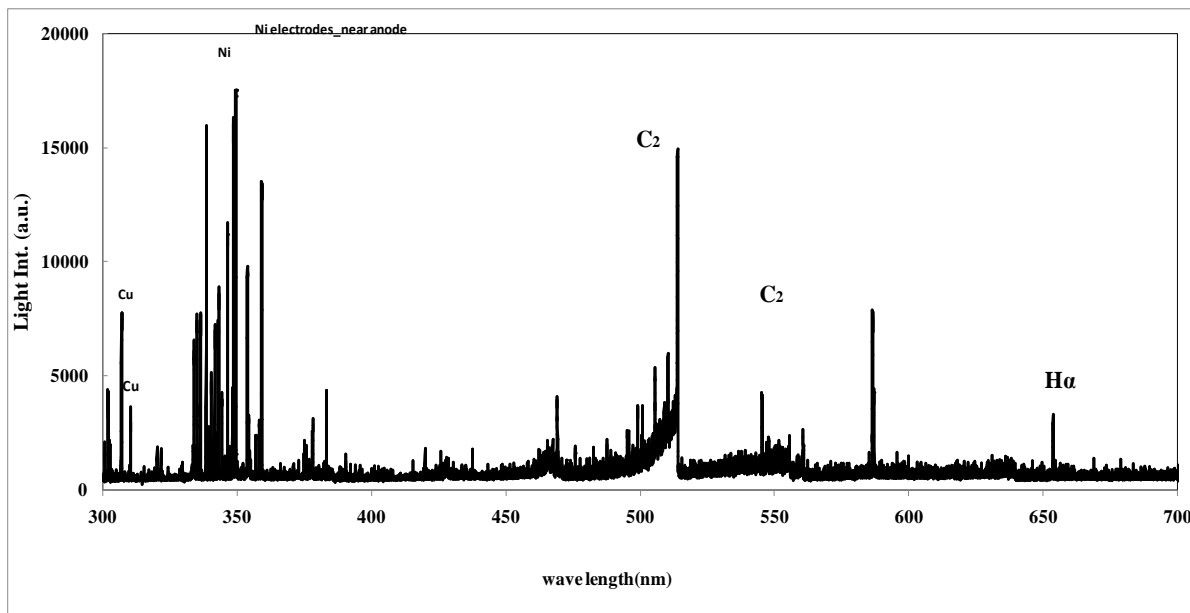

Figure 9. Light spectrum emitted from LPG discharge near the anode using Ni electrodes.

The most recognized spectra in **Figure 6** are C_2, CH, N_2 bands, H_α, Cu and Zn lines. The appearance of the emitted H_α line indicates the existence of hydrogen gas which is formed as natural subsequent of the dissociation of the hydrocarbon components in the above described discharge. The dissociative reactions will be discussed latter in section 3.4. Cu and Zn lines indicate the existence of the Cu and Zn atoms which are emitted from the brass electrode surface through the evaporation and sputtering processes. Emitted C_2 and CH bands are related to the existence of the C_2 molecule and CH radical which are formed as a result of the dissociation of propane and butane molecules. N_2 band confirms the existence of nitrogen molecules due to the existence of some N_2 impurities in the discharge tube and in the LPG gas cylinder.

Figure 7 shows the emitted light spectra from the LPG discharge near the anode, using brass electrodes. The most observed spectra near the cathode have been disappeared near the anode, except the N_2 band while C_2 bands are hardly detected. This difference between the two measured spectra can be explained as follows:

The main source of hydrogen atom (H_α line), C_2 molecule (C_2 band) and CH radical (CH band) are the dis-

sociation of propane and butane molecules. The data confirm that the dissociation processes occurs mainly near the cathode. The mean energy of the electrons in the discharge is much higher near the cathode rather than near the anode [8]. Also the spark discharge spots, formed on the cathode, elevate the propane and butane molecules temperature, which in turn enhances the thermal dissociation processes of propane and butane molecules. The resultant species (atoms, molecules and radicals) from the dissociation processes diffuse in all directions and hence their densities near the anode are too low to be detected in the measured spectrum.

Two types of the resultant species are expected; the first one is the unstable species such as hydrogen atoms and CH radicals, where both of them may react with other species to form more stable species such as hydrogen molecules H_2 and hydrocarbon molecules.

The second one is a stable species like C_2 molecules which may recombine together to form carbon clusters. The formed carbon clusters diffuse in all directions and then deposits on the electrodes and on the walls of the discharge tube. The deposition of carbon on the electrodes will be discussed later in section 3.3.

Figure 8 shows the emitted light spectra from LPG discharge near the nickel cathode surface where H_α, Cu and Ni lines are recognized. The Ni electrodes have been obtained by coating the brass electrodes with nickel. The intensity of H_α line using Ni cathode electrode is higher than that in the case of brass electrode. This can be related to the fact that Ni is working as good catalyst for the dissociation of the propane and butane molecules [16] [17]. Existence of Ni electrode and Ni atoms in the dissociation zone enhance the rate of dissociation process and hence increases the density of hydrogen atoms. Cu and Ni lines indicate the existence of Cu and Ni atoms which are emitted from cathode electrode as a result of the evaporation and sputtering processes. C_2, CH and N_2 bands are also recognized in **Figure 8** where their intensities are higher than that in the case of brass cathode electrode as a resultant of the effect of the Ni as a catalyst for the dissociation process. **Figure 9** shows the light spectrum emitted from LPG discharge near the anode using Ni electrodes. The H_α line and C_2 band near the anode have low intensity than near cathode. These spectra did not noticed for the brass anode. The appearance of H_α line and C_2 band near the anode can be attributed to the higher density of hydrogen and carbon molecules which are produced near the cathode region and hence diffuse to the anode. The intensity of the H_α line can be taken as an indicator to the density of the hydrogen atoms and hence to the high rate of the dissociation process. The intensity of the H_α line ($I_{H\alpha}$) can be expressed in the form [18]:

$$I_{H\alpha} = N_e N_H \langle Q_{H\alpha}(v_e) v_e \rangle \tag{1}$$

where N_e is the electron density, N_H is the hydrogen atoms density, $Q_{H\alpha}$ is the cross section of the excitation process of hydrogen atoms, v_e is the electron velocity and the symbol $<>$ indicates to the average of the product over a Maxwellian velocity distribution. **Figure 10** shows the relative intensity of H_α line as a function of the applied voltage. It cab seen that, the intensity of H_α line increases as the applied voltage increases, which can be attributed to the increase in the electron density N_e, the mean electron energy and hydrogen atom density N_H.
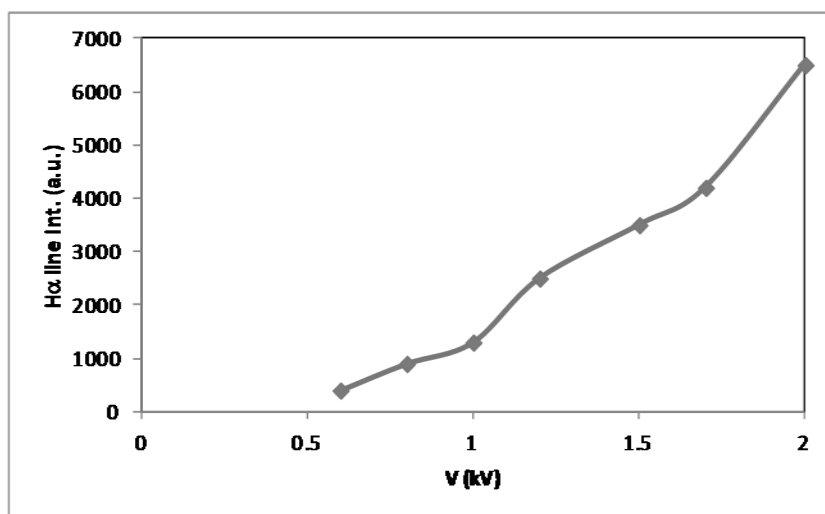

Figure 10. Relative intensity of the emitted H_α line as a function of the applied voltage.

4. Conclusion

The electric and spectroscopic characteristics of electric discharge have been used to explore the discharge mechanisms in LPG. A deviation from Paschen's law has been reported which has been attributed to the diffusion outside the discharge volume of the active species of secondary processes such as photons and excited atoms. The discharge has a repetitive behaviour where each cycle consists of three phases; discharge off, glow discharge and spark discharge. The repetition frequency of the discharge covers a wide range from 5 kHz to 5 MHz which depends on the applied voltage and the gas pressure. It is concluded that the present discharge modes are very useful for the dissociation of LPG molecules. Hydrogen atoms, C_2 molecule and CH radical have been detected in the discharge spectra using emission spectroscopy measurements. The dissociation processes are attributed to two processes; the electron collision with propane and butane molecules during the glow discharge mode and the gas heating due to the spark discharge mode. The dissociation process occurs mainly near the cathode surface wherein the electron density and the gas temperature are the highest. Besides working as a cathode, Ni electrode has been proven to be a good catalyst for increasing the dissociation rate of propane and butane molecules.

Acknowledgements

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