CHAPTER 2:

HISTORICAL INTRODUCTION ON LIQUID PETROLEUM GAS (LPG) SENSORS
ABSTRACT:

Hydrocarbon gases are being widely used as a fuel for domestic and in industry as a clean source of energy for burning. However, they are potentially hazardous because of the high possibility of explosion accidents caused due to leakage. This has resulted in an increased demand to develop sensors to detect these hydrocarbon gases. This chapter deals with the survey of work done towards the development of hydrocarbon gas sensors including Liquid Petroleum Gas (LPG) by various investigators using semiconducting oxides as base material.
The term liquefied petroleum gas (LPG), is applied to the hydrocarbons, the chief components of which are butane (70 to 80%), propane (5 to 10%) and propylene, butylene, ethylene, methane (1 to 5%). These hydrocarbons can be liquefied under moderate temperature and pressure, but they are gases under normal atmospheric conditions. Liquefied petroleum gas derived from natural gas contains saturated hydrocarbons (natural gas from some fields also contains unsaturated hydrocarbons). Where as those derived from oil refinery gases may contain varying low amounts of unsaturated (olefins) hydrocarbons. Manufactured gas is defined as combustible gas produced from coal, coke, or oil or by reforming of natural or liquefied petroleum gases.

Hydrocarbon gases, widely used in industrial and domestic fuels, have often proved to be potentially hazardous because of possible explosions which might be caused due to accidental leakage. This is the reason why there has been an increased demand for sensors to detect these hydrocarbon gases.

Sensing characteristics of tin (IV) oxide gas sensors prepared by screen printing method were studied [1]. The gas sensor was obtained by screen-printing a multi-layer structure with a paste obtained with SnO₂ (0.5 µ) prepared by direct precipitation. The sensitivity of the sensor was extended from H₂ and
alcohol to CO and isobutane by directly burying a Pt wire into the SnO$_2$ layer instead of printing with Au paste during electrode formation.

A semiconductor gas sensor was prepared by Yazaki Corp., Japan [2], with high sensitivity to CH$_4$ and suppressed sensitivity to alcohol and H$_2$. The sensor was prepared by sintering SnO$_2$ at 500 °C. SnO$_2$ coated was a mixture containing α or γ - Al$_2$O$_3$, Mn$_2$O$_3$, with particle size 1-2 μm; Pt, Pd or Rh or their oxides, and alumina binder.

Matsushita Electric Works Ltd. brought out a fuel gas sensor element [3], a combustible gas sensor [4] and a gas detector element [5]. This sintered sensor element consisted of In$_2$O$_3$, Fe$_2$O$_3$ and PdO for the equivalence sensitivity to the lower explosion limits of CH$_4$ in natural gases 5.6, isobutane in liquefied petroleum gases 1.8 and H$_2$ in city gas 4.0 volume percentage.

The sensitivity characteristics of SnO$_2$ based gas sensors prepared by sintering were also studied by Parn et al. [6] in the presence of CO and C$_3$H$_8$ gases. SnO$_2$ mixed with 1 wt.% La$_2$O$_3$ and PdCl$_2$ showed the highest sensitivity to CO and C$_3$H$_8$ at 250 °C.

A semiconductor gas sensor composition was developed by Hitachi Ltd.. [7] for combustible gases (CH$_4$, C$_3$H$_8$, H$_2$) consisting of an inorganic oxide mixture of SnO$_2$, NiO, and LaNiO$_3$ and glass. The composition has been found to have a stable service life and not affected by ethanol.
Matsushita Electronic Works Ltd., brought out a combustible gas sensor [4] consisting of a mixture of In$_2$O$_3$, SnO$_2$, PdO and of Rh$_2$O$_3$ and PtO$_2$ with the latter amount being less than that of the PdO. Thus a mixture of In$_2$O$_3$, SnO$_2$, PdO$_2$, PtO$_2$ and Rh$_2$O$_3$ was modulated into a cylindrical element with buried Pt electrodes and sintered at 600 °C for 1-3 hrs. The sensors have nearly equivalent sensitivities to H$_2$, CH$_4$ and C$_4$H$_{10}$.

The same company fabricated gas sensors [8,9] composed of In$_2$O$_3$, SnO$_2$ and PdO (0.5 - 5 wt. %) with a fine powdered solid obtained by co-precipitation of a solution containing, In$^{3+}$, Sn$^{4+}$ and Pd$^{2+}$. This method gives a solid with well-dispersed components, and is useful for fabrication of stable gas sensors for CH$_4$, C$_4$H$_{10}$ and H$_2$. Gas sensors composed of In$_2$O$_3$ (50-60 wt.%), SnO$_2$ (35-40 wt.%), PdO (0.1-5 wt.%) and PtO$_2$ (0.1-8 wt. %) were prepared. This showed stable sensitivity to CH$_4$, C$_4$H$_{10}$ and H$_2$. It is useful for leakage alarm devices.

Nippon Electronic Co. Ltd., [10] fabricated a gas sensor consisting of metal oxide semiconductor containing SnO$_2$ and platinum chloride, for an isobutane sensitive and a CH$_4$ sensitive metal oxide semiconductor containing SnO$_2$ and platinum chloride, for and isobutane sensitive and a CH$_4$ sensitive metal oxide semiconductor containing SnO$_2$ and Pd.

Hitachi Ltd., [11] fabricated a gas sensor consisting of powdered oxides of Sn, W and/or Zn (70-99.5 wt.%), V$_2$O$_5$ (0.5-10 wt.%), and glass (2.5-29.5 wt.%).
The semiconductor gas sensor showed high sensitivity and excellent resistance to mixture and corrosive gases. A paste of SnO$_2$ (95 wt.%), V$_2$O$_5$ (2.5 wt.%) and CaO-ZnO-PbO-TiO$_2$ glass (2.5 wt.%) was applied onto an Al$_2$O$_3$ substrate having an electrode and a heater, fired and then equipped with another electrode to give a gas sensor which had high sensitivity to CH$_4$.

Ricoh Co. Ltd., [12] fabricated a highly sensitive gas detector with low power consumption consisting of the following: (a) a substrate e.g. Si a heating layer having a bridge structure on the substrate, a pair of lead layers formed on the heating layers via an insulator layer (e.g. SiO$_2$) and a gas sensitive layer (e.g. a metal oxide semiconductor such as SnO$_2$, Fe$_2$O$_3$ or ZnO) formed between the pair of lead layers. The gas is detected on the basis of the change in resistance between the lead layers when the gas makes contact with the gas-sensitive layer. The detector is under a pulsed operation mode and is useful in the detection of liquefied petroleum or city gas.

Matsushita Electronic Works Ltd., [13] have fabricated a gas detector containing Fe$_2$O$_3$ and SnO$_2$ prepared by using a powder co-precipitated from an aqueous solution Containing Fe compound and Sn compound. The preferred Fe compounds were FeSO$_4$ and Fe$_2$(SO$_4$)$_3$, and the preferred Sn compounds are Sn(SO$_4$)$_2$ and SnCl$_4$. This method of preparation was reported to hinder the crystallinity of Fe$_2$O$_3$ particles, resulting in good storage stability. Thus a powder material was prepared by co-precipitating FeSO$_4$.7H$_2$O and Sn(SO$_4$)$_2$ at pH 6.5. The powder was pressed into disks having Pt electrodes, and then sintered at
600 °C to give a gas detector. The detector shows high sensitivity to CH₄, H₂ and alcohol even after subjecting to high temperature and high humidity conditions. They also developed a similar composition for a detector with increased CH₄ sensitivity and reduced H₂ and alcohol sensitivity, resulting in good sensitivity balance [14].

Sensors were also made for detecting underground combustible gas [15]. A semiconductor sensor was made from SnO₂ dispersed inside the cylindrical case, and a gas permeable waterproof membrane placed on the surface of the cap. The sensor is inserted inside a drilled hole in the ground to measure the concentration of combustible gases (e.g. CH₄) in the free or dissolved state in underground water.

Combustible gas sensors with fire alarming function consisting of semiconductor gas-sensing element [16], a temperature-detecting element, and an input combining operator for temperature compensated gas detection as well as temperature rise detection. Thus LaNiO₃, WO₃ and SnO₂ pastes were separately printed besides paste for thermistor, over a printed and sintered electrode on a base board having a heater on the other side and then a paste for another electrode was printed over the elements and sintered. The WO₃ element reacts strongly with alcohol, H₂ and CO but the LaNiO₃ element with only alcohols and SnO₂ element with alcohols, H₂, smoke and CH₄. By the combination of the 3 elements and a thermistor, the type of gas, smoke and temperature rise were differentiated in the detection.
Combustible gas sensor elements were prepared by Kanagawa [17] as follows. A combustible gas sensor element of sintered SnO$_2$ and/or ZnO containing an additive component and also a gas sensor element having a small temperature resistance coefficient was provided from a mixture containing SnO$_2$ (92.6 wt. %), OsO$_4$ (1.4 wt. %) a sintering agent (1.0 wt. %) and glass (5.0 wt.%). A temperature compensation element having a similar temperature resistance coefficient was provided from a mixture containing SnO$_2$ (93 wt.%), PdCl$_2$ (1 wt.%), a sintering agent (1 wt. %), glass (5 wt.%), and OsO$_4$ (1.4 wt.%). Both the elements were printed together on a baseboard to form a bridge circuit and sintered at 650-800 °C to prepare a gas sensor. Gas detecting sensitivity of the above-prepared sensor for C$_3$H$_8$ was not affected by changes of detection power source or atmospheric temperature.

Nakamura Yuji et al.[15] fabricated a combustible gas sensor element prepared with SnO$_2$, which has a primary grain size of 150-250 Å. Thus Sn(OH)$_4$ was precipitated from a SnCl$_4$ solution with NH$_4$OH, decanted and then a PdCl$_2$ solution was added to the precipitate to give SnO$_2$: Pd. The mixture was dried at 200 °C and calcined at 550 °C. The powder was milled to a proper particle size, and then formed to a paste for sensor element production having 150-250 Å grain size. The paste was dried and calcined for 0.5 hr at 725 °C to prepare a sensor element for CH$_4$ leak detection and alarm.
A method has been described for preparing a paste by milling the powder to that required particle size [19] for making reducing gas sensors from which the gas-sensitive working layer of a semiconductor gas sensor is formed. The method induces pre-aging of stannic acid for 30 days at 50 °C in an oxygen poor atmosphere to prepare it for use in the paste. The resulting sensors have a high sensitivity to hydrocarbon gases (e.g. CH₄) and exhibit stability. Applications in breath alcohol testing exhaust gas monitoring and home gas alarms are also indicated.

Stannic oxide semiconducting gas sensor was also prepared by wet coating process [20]. They mainly comprise of SnO₂-In₂O₃-MgO coatings with PdO, La₂O₃, ThO₂, NiO and Nb₂O₅ as dopants. There is another sensor applicable for all kinds of city gases including CO gas with remarkably high sensitivity [21]. Another group of researchers reported [22] a detector based on conductivity changes in the presence of gases and humidity along with its method of production. The semiconductor additive materials are selected for specific detection, e.g. TiO₂-V₂O₅-Pd (humidity), SnO₂-Pt (NH₃), SnO-Pd (C₆H₆), ZnO-V₂O₅-Ag (EtOH).

Further, films of tin oxide were also studied [23] for sensing H₂ gas as well as CH₄, C₂H₆, C₄H₈ and O₃ gases. Thus a SiO₂ layer was formed on a Si wafer at 100 °C for 2 hr in an atmosphere of H₂O and O₂, followed by the formation of a SnO₂ film (140 Å) on the SiO₂ layer by a vapor deposition method. Finally, 2 Pt electrodes (1 μm) layed by a vapor deposition technique were formed on the
SnO₂ film. The sensor element showed excellent performance in detecting CH₄ in dry air containing 0.1% CH₄ and H₂ in dry air.

Literature also shows that until now metal oxides such as SnO₂ and Fe₂O₃ have been very popular as base raw materials for making hydrocarbon-sensing devices [24,25]. The gas sensors have also been fabricated by the process of screen printing of thick film paste of Fe₂O₃ without any other catalyst. This particular device showed a high sensitivity to hydrocarbon gases. Their further studies showed that addition of palladium (Pd) as catalyst to Fe₂O₃ enhanced the sensitivity, and selectivity to hydrocarbon gases. This addition of Pd resulted in an increase in resistance, which was later lowered by an addition of SnCl₄ 5H₂O without impairing the sensitivity to the hydrocarbon gases. Their studies gave the optimum composition of a 0.5 wt. % of SnCl₄ 5H₂O and 1 wt.% of Pd in Fe₂O₃ sintered at 400 °C for 2 hrs, for the detection of hydrocarbon gases at an operating temperature of 300 °C.

Paryńczuk et al. [26] studied the dependence of the sensitivity of hydrocarbons on SnO₂ sensors, it is shown to increase with chain length and decrease with hydrocarbons having double bonds. A high selectivity for hexane was reported.

On the other hand ultra micro particles of SnO₂-TiO₂ complex oxides doped with Pt as a catalyst and Sb as a conductive dopant was prepared by coprecipitation method [27]. The sensors were fabricated by screen printing
method. They observed; (a) 1 wt.% of Sb addition of the thick films lowered the resistance of the thick film by around 2 orders of magnitude without serious loss of gas sensitivity. (b) TiO$_2$ was finely dispersed on SnO$_2$ grains with enhanced sensitivities to hydrocarbon gases when the loading rate was 3-5 mol.%.

Raju et al. [28] reported a gas sensor containing V$_2$O$_5$ supported on ZrO$_2$ that has been found to be an excellent sensor for LPG at 625 k. In situ x-ray diffraction studies showed that V$_2$O$_5$ was reduced to VO$_2$ with a metastable monoclinic structure on contact with the hydrocarbons and was oxidized back to the parent oxide on exposure to air.

Plog et al. [29] used zeolite as a coating of planar interdigital capacitive sensor for hydrocarbons.

Saito et al. [30] measured the changes in resistivity and chemical changes in porous ZnO and PtZnO ceramics in reducing gases at 300 and 400 °C. Their results show that platinum-added ZnO is more sensitive to hydrocarbons than to CO or H$_2$. The reaction sequences for the gas sensing process has been proposed, taking into account partially oxidized intermediates of hydrocarbons and oxidation of Pt without an electron transfer process.

Nitta et al. [31] reported that the performance of SnO$_2$ based sensors for detection of propane can be improved by doping SnO$_2$ with V, Nb, Ti or Mo. These sensors can be used for reliable detection of propane in the concentration range 0.2 - 0.5 %.
Raju [32] studied the gas sensing characteristic of $\gamma$-Fe$_2$O$_3$ wafers toward various gases and vapours at different temperatures. He claimed that maximum sensitivity for LPG is 0.9 around 600 K.

Ishii Takashi et al [33] developed a thick film gas sensor to detect LPG, city gas and hydrogen comprising of two alternate oxidation layers and a gas sensitive layer in between. The gas sensitive layer is made from an n-type semiconductor such as SnO$_2$ and the oxidation layers are made from SnO$_2$ along with a noble metal and a metal oxide like NiO.

Kubota Kazunami [34], Ichimura Takeshige et al [35] simultaneously reported sensors based on tin oxide, oxidation catalyst layer of Mn-oxide loaded Al$_2$O$_3$ on the surface and a heater for maintaining the temperature. This device is found to sense i-C$_4$H$_{10}$ with very high sensitivity compared to ethanol over a wide temperature range and hence it has found wide use in alarm systems to detect LPG.

Xu et al [36] studied the effect of Al doping on tin dioxide based elements. Gas sensitivity to H$_2$ and i-C$_4$H$_{10}$ was found to be promoted extensively. They studied the Seebeck coefficient and showed that carrier concentration decreased with Al doping. The crystallite size was also found to decrease with Al doping. It was concluded that the increase in Debye length and decreased crystallite size were combined to produce the microstructure responsible for extensively high gas sensitivity of 1 and 5 % Al doped elements.
Kubota Kazumi [37] also reported a Sn-oxide electrically connected to a pair of electrodes on the surface of a substrate and an electrical heater on the back of the substrate. The surface of the gas sensing body has an oxide catalyst layer containing a mixture of Pt and Fe oxide or Ni oxide. The sensor has a stable and high sensitivity to isobutane and is used for preventing misinformation of LPG leak caused by ethanol.

Sandberg et al. [38] reported a distributed cross-linked sensor that not only detects a leak of gasoline, diesel and other hydrocarbons, but also the location of leak. This instrument can be extended to hundreds of feet and is a useful tool in the extension of leak detection from a point system to a distributed system.

Chung Wan-Young [39] showed that addition of TiO₂ improved the characteristics of SnO₂ based thick film gas sensors prepared by screen printing technology for some hydrocarbon gases. SnO₂ was prepared by co-precipitation and dried by hot air in a gravity convection oven or by freeze drying method. They also observed that the phase change from anatase to rutile affects the gas sensitivity. Pt in the form of H₂PtCl₆ induced during co-precipitation improved the sensitivity to hydrocarbons.

Chung Wan-Young et al. [40] fabricated silicon IC technology based SnO₂ microsensor for monitoring LPG. The whole chip 9 mm x 9 mm consists of 9 sensors. Each sensor is supported by a thin film member of SiO₂/Si₃N₄/SiO₂ layers that provides a low thermal mass and prevents heat conditions through the
surrounding substrate material. Thermal evaporation of metallic Sn granules and subsequent thermal oxidation of the metallic film to SnO₂ thin films at 800 °C. They formed the SnO₂ (Pt) thick film with a layer of Pt with a thickness of several tens of Å sputtered onto the tin oxide film and heat-treated at 500 °C in air. The microsensor is reported to exhibit 85 and 92% sensitivities to 5000 ppm C₃H₈ and C₄H₁₀ at 250 °C respectively and a response time of less than 5 seconds.

Phani et al [41] reported a composition SnO₂/Al₄Si₂O₇/Pd as an efficient LPG sensitive material. The same authors [42] also studied the electrical response of noble metal (Pt and Pd) doped SnO₂ to improve the selectivity for LPG. Cross sensitivity to other interfering gases like CO and CH₄ were also studied at an operating temperature of 350 °C. They report XPS, XRD studies for the structure, chemical composition and crystallite size. They suggest the possible application of this composition as a LPG detector.

Kurzweil et al [43] observed changes in conductance and capacitance of zeolite that allow concentration of butane, NH₃ and other gases to be distinguished by zeolite interdigital sensors. By impedance spectroscopy, hydrocarbon conversion can be separated from the effect of H₂O, NaY-Zeolite shows a moderate conductance, which is due to the mobility of Na and is influenced by the presence of gases adsorbed at the pore surfaces.
Zhang et al [44] reported an amorphous SnO$_2$-La$_2$O$_3$ based sensor, which detects CO and LPG selectively at 96 and 295 °C respectively. A second sensor composed of SnO$_2$-ZrO$_2$ detects CO and H$_2$ at 70 and 375 °C respectively.

Floser et al [45] report a hydrocarbon sensitive sensor element arranged in a tightly sealed apparatus with a membrane some distance from it for detection of hydrocarbons especially in fluid medium. The hydrocarbon in the liquid passes through the membrane and into the chamber behind the membrane. A gas permeable sintered metal plate is installed between the membrane element and the hydrocarbon-sensing element. This apparatus is especially useful in exploring petroleum and natural gas at the bottom of the ocean.

Chaudhary et al [46] demonstrate that a surface functionalised gas sensing material is capable of better sensitivity and selectivity to hydrocarbons by grafting some RU-O linkages on the surface of tin oxide. They showed an increase in sensitivity from 4 to 320 at 300 to 1000 ppm LPG after this surface modification.

To overcome the difficulty in determining which new metal oxide materials be useful for carbon monoxide or hydrocarbon sensors, a rapid evaluation process using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) has been developed by Kevin et al [47]. Three basic response modes, absorptive, electrochemical and thermistor are herein described for metal-oxide materials.
Semiconductor gas sensors, which have reduced power consumption, as low as 100 mW developed for the application for portable gas detection devices were reported by Kim et al [48]. The sensors were fabricated with a base material of tin dioxide and 4 wt.% Pd dopant using thick film technology.

Lin yong-Jing et al [49] fabricated an array composed of 16 metal oxide semiconductor gas sensors to analyze gas mixture quantitatively. The responses of sensor array to C$_2$H$_6$, propane, propylene were treated three-layer artificial neural networks (ANN) with the method of error bulk propagation and partial least squares (PLS). The pattern recognition results indicated that the concentration predicted with ANN is better than with LPLS.

A highly sensitive and selective sensor based on an oxygen deficient spinel; ZnGa$_2$O$_4$ has been studied by Satyanarayana et al [50] for the detection of Liquefied petroleum gas sensor. This sensor operates at 320 °C and shows a change of 4-5 orders in the resistance when exposed to the gas. The sensor is insensitive to the presence of CO and CH$_4$ at this operating temperature.

A highly sensitive LPG gas sensor was prepared by C.V. Gopal Reddy et al [51] based on BaSnO$_3$. Their results show that addition of small amounts of noble metals such as Pt, Pd, Rh, Ru and Ag to BaSnO$_3$ promotes not only the gas sensitivity but also improves the rate of response towards LPG. Change of gas sensor characteristics before and after the exposure to the different test gases like LPG, CO and CH$_4$ has been explained on the basis of work function of metal additives.
Sergio Nicoletti et al [52] developed Tin oxide based thin film sensors for aromatic hydrocarbon detection. The sensors were exposed to gas mixtures containing benzene, wet synthetic air, and CO, with 0.5 ppm of benzene added to 30% relative humidity synthetic air and 20 ppm CO. The sensing layers show good response to benzene concentration as low as 0.5 ppm.

A mixed-potential hydrocarbon sensor using a SrCe 0.95 Yb 0.5 O₃ electrolyte with a Pt electrode was prepared by Ken-taro Mori et al [53]. They mainly investigate a relationship between the sensing properties for hydrocarbons and ion conduction in the electrolyte under oxidizing conditions. There was an increase in the mixed potential for propene with increasing proton conduction or decreasing oxide ion conduction. The resulting sensor showed an enhanced mixed potential for C1-C4 hydrocarbons by increasing the carbon number, unsaturating the C-C linkage, and branching the chain structure.

Recently Jinzhong Wang et al [54] developed a thick film gas sensor to detect LPG and hydrogen gas based on γ-Fe₂O₃. Their results show that among the various metal oxide additives, Ag₂O is outstanding in promoting the sensing properties of γ-Fe₂O₃ element to H₂ in air. The γ-Fe₂O₃ element loaded with 6 wt.% Ag₂O is very sensitive to H₂ at 320 ºC, while it is also sensitive to many other gases, especially C₂H₅OH. The element is highly sensitive and selective to LPG and H₂, after it is modified with the surface-coat of Al₂O₃ containing 1.5 wt.%
PtO. The response of this element to \( \text{C}_4\text{H}_{10} \) and \( \text{H}_2 \) is rather rapid. So the element is very useful to detect the leakage of coal gas or LPG in domestic appliances.

Beside these many researchers [55 - 64] have also been worked on hydrocarbon gas sensors.
REFERENCES:


24. D. D. Lee and W. T. Chang,

25. D. D. Lee and D. H. Choi,


27. W. Y. Chang and D. D. Lee,

28. A. R. Raju and C. N. R. Rao,

29. C. Plog, W. Maunz, P. Kurzweil, E. Obermeier, C. Scheibe,

30. S. Saito, M. Miyayama, K. Koumoto and H. Yanagida,

31. M. Nitta, S. Kanefusa and M. Haradome,

32. R. Raju, Ph.D. Thesis,


36. Xu, Chaonan; Yamaki, Jun; Miura, Norio; Yamazoe, Norio, 


39. Chang Wan Young, Lee Duk Dong and Sohn Byung Ki, 

40. Chung Wan-Young, Shim Chang-Hyun, Choi Soon-Don, and 
Lee Duk-Dong, 

41. A. Ratna Phani, 
Ph. D. Thesis, 


43. P. Kurzweil, W. Maunz, C. Plog, 


46. V. A. Chaudhary, I. S. Mulia, S. R. Sainkar, A. A. Belhekar, 
K. Vijaymohanan, 

47. K. W. Kirby and H. Kimura, 


53. Ken-taro MORI, Takashi HIBINO, Atsuko HASHIMOTO and Mitsuru SANO.


T. Oyabu,

S. C. Chang,

Y. K. Fang and J. J. Lee,

D. D. Lee and W. Y. Chung,

J. Mizsei,

G. Sberveglieri, S. Groppelli and P. Nelli,

G. Sberveglieri, G. Faglia, S. Groppelli and P. Nelli,