2013

Thermal Conductivity Sensors in Automotive Applications

Weijun Deng
University of Windsor

Follow this and additional works at: https://scholar.uwindsor.ca/etd

Recommended Citation
https://scholar.uwindsor.ca/etd/4969

This online database contains the full-text of PhD dissertations and Masters' theses of University of Windsor students from 1954 forward. These documents are made available for personal study and research purposes only, in accordance with the Canadian Copyright Act and the Creative Commons license—CC BY-NC-ND (Attribution, Non-Commercial, No Derivative Works). Under this license, works must always be attributed to the copyright holder (original author), cannot be used for any commercial purposes, and may not be altered. Any other use would require the permission of the copyright holder. Students may inquire about withdrawing their dissertation and/or thesis from this database. For additional inquiries, please contact the repository administrator via email (scholarship@uwindsor.ca) or by telephone at 519-253-3000 ext. 3208.
THERMAL CONDUCTIVITY SENSORS IN AUTOMOTIVE APPLICATIONS

by

Weijun Deng

A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of Electrical and Computer Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science at the
University of Windsor

Windsor, Ontario, Canada

2013

© 2013 Weijun Deng
Thermal Conductivity Sensor in Automotive Applications

by

Weijun Deng

APPROVED BY:

______________________________________________
X. Nie
Department of Mechanical, Automotive and Materials Engineering

______________________________________________
N. Kar
Department of Electrical and Computer Engineering

______________________________________________
J. Wu, Advisor
Department of Electrical and Computer Engineering

______________________________________________
M. Zheng, Advisor
Department of Mechanical, Automotive and Materials Engineering

10 September 2013
DECLARATION OF ORIGINALITY

I hereby certify that I am the sole author of this thesis and that no part of this thesis has been published or submitted for publication.

I certify that, to the best of my knowledge, my thesis does not infringe upon anyone’s copyright nor violate any proprietary rights and that any ideas, techniques, quotations, or any other material from the work of other people included in my thesis, published or otherwise, are fully acknowledged in accordance with the standard referencing practices. Furthermore, to the extent that I have included copyrighted material that surpasses the bounds of fair dealing within the meaning of the Canada Copyright Act, I certify that I have obtained a written permission from the copyright owner(s) to include such material(s) in my thesis and have included copies of such copyright clearances to my appendix.

I declare that this is a true copy of my thesis, including any final revisions, as approved by my thesis committee and the Graduate Studies office, and that this thesis has not been submitted for a higher degree to any other University or Institution.
ABSTRACT

Over the last decade, there has been a growing research interest in the on-board fuel generated hydrogen in automotive application. In this thesis, in order to find a suitable sensor to work in a complex gas mixture, currently commercialized hydrogen sensors have been compared. Furthermore, a thermal conductivity sensor has been selected and studied. The concentrations of hydrogen, nitrogen and carbon monoxide gas mixtures were simulated in Matlab. Simulation results demonstrate that the thermal conductivity of the gas mixture is measurable. Carbon monoxide, which is as a main interference gas to the hydrogen detection, does not influence the detecting. Moreover, experiments have also been conducted by using thermal conductivity sensor, bottled hydrogen, carbon monoxide and nitrogen gas mixtures. Up to 7 liter-per-minute gas flows and zero drift were tested in these experiments. The results obtained from these experiments are very similar to that of the simulation.
ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my supervisors Dr. Q.M. Jonathan Wu and Dr. Ming Zheng, who not only provided me with a good experimental environment and sophisticated experimental setup, but also encouraged me with their great kindness and patience. All of this support enabled me to finish this thesis successfully.

Also, I would like to thank my thesis committee members, Dr. Narayan Kar and Dr. Xueyuan Nie, for giving me constructive criticism and helping me improve my thesis. In addition, I would like to thank Dr. Meiping Wang and Marko Jeftic for discussing and sharing their ideas and suggestions with me. Without their support, it would have been hard for me to finish this project on time.

Finally, I would like to thank Dr. Bill Zhou for allowing me using his laboratory to do some of my experiments.
# TABLE OF CONTENTS

DECLARATION OF ORIGINALITY .................................................................................. iii

ABSTRACT .................................................................................................................. iv

ACKNOWLEDGEMENTS ............................................................................................. v

LIST OF TABLES ........................................................................................................... ix

LIST OF FIGURES ........................................................................................................ xi

LIST OF ABBREVIATIONS ........................................................................................... xiii

CHAPTER 1 INTRODUCTION ......................................................................................... 1
  1.1 Background ........................................................................................................... 1
  1.2 Hydrogen Safety ................................................................................................... 3
  1.3 Hydrogen Concentration ....................................................................................... 3
  1.4 Hydrogen Sensors ................................................................................................ 4
  1.5 Thesis Organization .............................................................................................. 5

CHAPTER 2 LITERATURE REVIEW .............................................................................. 7
  2.1 Hydrogen Sensors in Automotive Applications ................................................... 7
  2.2 Currently Commercialized Hydrogen Detecting Mechanisms and Sensors .......... 8
    2.2.1 Catalytic Sensors ........................................................................................... 9
    2.2.2 Electrochemical Hydrogen Sensors ................................................................. 10
    2.2.3 MOx Hydrogen Sensors .................................................................................. 11
    2.2.4 Thermal Conductivity Sensors ....................................................................... 12
  2.3 Comparison of the Sensors .................................................................................. 13
  2.4 Comparison Results ............................................................................................ 16
  2.5 Principles of Thermal Conductivity Sensors ....................................................... 17
  2.6 Thermal Conductivity of Hydrogen ..................................................................... 18

CHAPTER 3 SIMULATION RESULTS AND ANALYSIS ............................................. 20
  3.1 Hydrogen Detection by Thermal Conductivity Measurements ......................... 20
  3.2 Thermal Conductivity Calculation ........................................................................ 20
CHAPTER 4 EXPERIMENTS DESIGN .................................................................37
  4.1 Purpose of the Experiments ..............................................................37
  4.2 Description of the Experiments ..........................................................37
  4.3 System Design for the Experiments ....................................................38
    4.3.1 Detection Module .................................................................39
    4.3.2 Interface Module ..................................................................40
    4.3.3 Control Module ..................................................................41
  4.4 Experimental Setups ...........................................................................41
    4.4.1 Experimental Setup 1 .............................................................42
    4.4.2 Experimental Setup 2 .............................................................44
    4.4.3 Experimental Setup 3 .............................................................46
  4.5 Steps of Operation .............................................................................47

CHAPTER 5 EXPERIMENTAL RESULTS AND ANALYSIS ..........................49
  5.1 Results and Analysis of Experiment 1-Tested in Static [H2+N2] Gases ....49
  5.2 Results and Analysis of Experiment 2-Tested in Static [H2+CO+N2] Gases ......55
  5.3 Results and Analysis of Experiment -Tested in [H2+N2] Gas Flows ............59
    5.3.1 Tested in 5% Hydrogen Gas Flow ..........................................60
    5.3.2 Tested 10% Hydrogen Gas Flow .............................................62
    5.3.3 Tested in 30% Hydrogen Gas Flow ..........................................63
    5.3.4 Tested in 99.99% Hydrogen Gas Flow ......................................64
    5.3.5 The Experimental Result and Analysis of Experiment 3 .................65
5.4 Experiment 4-Tested at Constant Temperatures and Constant RH..................67
5.5 Experiment 5-Zero Drift.............................................................................72

CHAPTER 6 CONCLUSIONS AND FUTURE WORK ............................................74
6.1 Summary of Contributions ........................................................................74
6.2 Future Work ...............................................................................................77

REFERENCES .....................................................................................................79

VITA AUCTORIS ...............................................................................................86
LIST OF TABLES

Table 1: General characteristics of electrochemical sensors .............................................. 14
Table 2: General characteristics of MO\textsubscript{X} sensors ....................................................... 14
Table 3: General characteristics of thermal conductivity sensors ............................................. 15
Table 4: General characteristics of catalytic sensors ................................................................. 15
Table 5: The comparison based on datasheets of commercially available sensors ........... 16
Table 6: Basic constants used for calculation at 26.7 °C .......................................................... 23
Table 7: Examples of gas thermal conductivities at various temperatures ......................... 24
Table 8: Calculated results of H\textsubscript{2} and N\textsubscript{2} mixture at 300 K ........................................ 27
Table 9: Calculated results of H\textsubscript{2}, CO and N\textsubscript{2} mixture at 300 K .......................... 29
Table 10: [H\textsubscript{2} + CO + N\textsubscript{2}] vs. [H\textsubscript{2} + N\textsubscript{2}] at 300 K ........................................... 30
Table 11: Calculated results-10% H\textsubscript{2} and (0%~90%) CO in N\textsubscript{2} ............................. 32
Table 12: Calculation results of H\textsubscript{2} vs. CO\textsubscript{2} ................................................................. 35
Table 13: Descriptions of experiments ....................................................................................... 38
Table 14: Setup 1–hardware ........................................................................................................ 42
Table 15: Setup 1–gases ............................................................................................................... 43
Table 16: Setup 2–hardware ........................................................................................................ 45
Table 17: Setup 2–gases ............................................................................................................... 45
Table 18: Setup 3–hardware ........................................................................................................ 46
Table 19: Results of experiment 1 .............................................................................................. 52
Table 20: Calculated results of the unit-removed values of experiment 1 .......................... 54
Table 21: Results of experiment 2 at 24°C±3°C ................................................................. 57
Table 22: Calculated results of the unit-removed values of experiment 2 .................... 58
Table 23: Parameters for calculating Re .................................................................................... 60
Table 24: Results of experiment 3 at 24°C±3°C ................................................................. 65
Table 25: Results at 31±2.3 °C while RH varied from 37% ~61% ........................................ 67
Table 26: Results at 26.5±1.5 °C while RH varied from 68% ~78% ~73% ....................... 68
Table 27: Results at 24.4±0.5 °C while RH varied from 72% ~ 56% ............................... 69
Table 28: Results at 62%±1% RH while temperature varied from 33.2 °C ~ 27.0°C ..... 70
Table 29: Zero drifts while temperature varied ............................................................... 73
Table 30: Voltages per 1% hydrogen ............................................................................. 73
LIST OF FIGURES

Figure 1: Ontario nitrogen oxides emissions in 2010 .................................................. 2
Figure 2: Currently commercialized H\textsubscript{2} sensor examples........................................ 8
Figure 3: Schematic of a typical catalytic type combustible gas sensor ................................. 9
Figure 4: Schematic of an electrolytic type H\textsubscript{2} sensor .................................................. 11
Figure 5: An example circuit of a thermal conductivity type H\textsubscript{2} sensor ......................... 12
Figure 6: Gas relative thermal conductivity with temperature ................................................. 19
Figure 7: The thermal conductivities of gases for simplification at 26.7 °C ............................... 25
Figure 8: Calculation of H\textsubscript{2} and N\textsubscript{2} mixture at 300 K ........................................... 27
Figure 9: Calculations of H\textsubscript{2}, CO and N\textsubscript{2} mixture at 300 K ................................. 29
Figure 10: [H\textsubscript{2} + CO + N\textsubscript{2}] vs. [H\textsubscript{2} + N\textsubscript{2}] gas mixture at 300 K .................. 31
Figure 11: Calculated results-10% H\textsubscript{2} and (0%~90%) CO in N\textsubscript{2} gas mixture ............... 33
Figure 12: Calculation results of H\textsubscript{2} vs. CO\textsubscript{2} ............................................................ 34
Figure 13: Block diagram of the detecting system .................................................................. 39
Figure 14: Setup 1–connections ......................................................................................... 43
Figure 15: Flow meter in the setup ..................................................................................... 44
Figure 16: Setup 2–connections ......................................................................................... 46
Figure 17: Steps of operation–static ................................................................................... 47
Figure 18: Steps of operation–gas flow ................................................................................. 48
Figure 19: Experimental outputs–5% H\textsubscript{2} ................................................................... 49
Figure 20: Experimental outputs–10% H\textsubscript{2} ................................................................ 50
Figure 21: Experimental outputs–30% H\textsubscript{2} ................................................................ 51
Figure 22: Experimental outputs–99.99% H\textsubscript{2} ................................................................ 51
Figure 23: Results of experiment 1 ..................................................................................... 52
Figure 24: The calculated values vs. experimental values of experiment 1 ......................... 54
Figure 25: Experimental outputs in 10% H\textsubscript{2} and 2% CO .............................................. 55
Figure 26: Experimental outputs in 10% H\textsubscript{2} and 5% CO .............................................. 56
Figure 27: Experimental outputs in 10% H\textsubscript{2} and 15% CO ............................................ 57
Figure 28: Results of experiment 2 ..................................................................................... 58
Figure 29: The calculated values vs. experimental values of experiment 2 .................. 59
Figure 30: 5% H₂ gas flow with flow rates from 0 ~ 7 LPM at 24°C±3°C ....................... 61
Figure 31: 10% H₂ gas flow with flow rates from 0 ~ 7 LPM at 24°C±3°C ...................... 62
Figure 32: 30% H₂ gas flow with flow rates from 0 ~ 7 LPM at 24°C±3°C ..................... 63
Figure 33: 99.99% H₂ gas flow with flow rates from 0 ~ 7 LPM at 24°C±3°C .................. 64
Figure 34: Flow rate vs. output voltages of different concentrations of H₂ ....................... 66
Figure 35: Output voltage change rate in 7 LPM gas flow ........................................... 66
Figure 36: Outputs vs. RH at 31°C .............................................................................. 68
Figure 37: Outputs vs. RH at 26.5°C ............................................................................ 69
Figure 38: Outputs vs. RH at 24.4°C ............................................................................ 70
Figure 39: Outputs vs. temperature at 62% RH ......................................................... 71
Figure 40: Zero drifts at R.H.=28.6%±0.2% ................................................................. 73
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC</td>
<td>analog to digital converter</td>
</tr>
<tr>
<td>CANBus</td>
<td>control area network bus</td>
</tr>
<tr>
<td>$D_H$</td>
<td>the hydraulic diameter of the pipe</td>
</tr>
<tr>
<td>EGR</td>
<td>exhaust gas recirculation</td>
</tr>
<tr>
<td>HC</td>
<td>hydrocarbon</td>
</tr>
<tr>
<td>LDL</td>
<td>lower detection limit</td>
</tr>
<tr>
<td>LFL</td>
<td>lower flammable limits</td>
</tr>
<tr>
<td>LPM</td>
<td>liter per minute</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight, g/mol</td>
</tr>
<tr>
<td>MCU</td>
<td>a micro-controller unit</td>
</tr>
<tr>
<td>MOx</td>
<td>metal-oxide semiconductor</td>
</tr>
<tr>
<td>NOx</td>
<td>nitric oxide and nitrogen dioxide</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>$P_c$</td>
<td>critical pressure, bar</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$T_c$</td>
<td>critical temperature, K</td>
</tr>
<tr>
<td>$T_r$</td>
<td>the reduced temperature</td>
</tr>
<tr>
<td>TC</td>
<td>thermal conductivity</td>
</tr>
<tr>
<td>TCS</td>
<td>thermal conductivity sensor</td>
</tr>
<tr>
<td>$V_{cal}$</td>
<td>calculated value</td>
</tr>
<tr>
<td>$V_{mea}$</td>
<td>the measured value</td>
</tr>
<tr>
<td>$V_{S,CAL}$</td>
<td>a set of calculated values</td>
</tr>
</tbody>
</table>
$V_{S\_MEA}$ a set of measured values

$V_{ur\_cal}$ unit removed value of calculated value

$V_{ur\_mea}$ the unit-removed value of the measured value

atm atmospheric pressure

ppm parts per million

$v$ mean velocity of the fluid

vol. volume

$y_i$ mole fraction of components $i$

$y_j$ mole fraction of components $j$

Greek letters

$\Gamma$ the reduced, inverse thermal conductivity

$\epsilon$ 1.065 numerical constant near unity for non-polar gases

$\lambda_i$ thermal conductivity of component gas $i$

$\lambda_m$ thermal conductivity of the gas mixture

$\lambda_{tr}$ monatomic value of the thermal conductivity

$\rho$ the density of the fluid

$\mu$ the dynamic viscosity of the fluid
CHAPTER 1
INTRODUCTION

1.1 Background

Hydrogen is the most abundant element, comprising about three quarters of the mass in the universe. It is also the simplest element which is only made up of one proton and one electron [34]. This makes hydrogen the lightest of all elements. It is fourteen times lighter than air, and it is colorless, odorless and tasteless. It does not produce acid rain, deplete the ozone or produce harmful emissions, and the only product after it has been oxidized by oxygen is water, so hydrogen has already been adopted in automotive applications for some years by these features (automotive research has been done). In potential automotive applications, hydrogen can be used:

- As a fuel to produce electricity, like in a fuel cell reactor [33].
- As an additional fuel to reduce emissions, like exhaust gas recirculation (EGR) reforming [1, 40, 41, 42].

A lot of research has been done on developing vehicles that use pure hydrogen gas or a hydrogen-rich gas as an energy carrier. The gas is either stored in a compressed gas tank in the trunk or under the back seat of the vehicle, or is produced on-board in a reforming process [36]. It is transported at a high pressure level via pipelines to a fuel cell module which produces the power to move the vehicle. When hydrogen is used as an additional fuel together with the hydrocarbon fuel, it has been proved to be effective in
reducing both soot and NOx (nitrogen dioxide and nitric oxide) emissions [1, 2, 4, 5, 51-55].

For example, on the air quality report prepared by The Ministry of the Environment of Ontario, the nitrogen oxide emission from road vehicles contributed 25% of the total among the total Ontario nitrogen oxides emission in 2010 [3]. It is one of the major sources of the nitrogen oxide emission as can be seen in Figure 1. NOx is a source of the formation of ground level ozone which has negative effect on human health [37, 38]. Thus, NOx reduction in the vehicle engine emission is one of the attractive researches which researchers are interested in.

Figure 1: Ontario nitrogen oxides emissions in 2010 [3]
1.2 Hydrogen Safety

As a fuel, hydrogen safety is very important. Hydrogen is not inherently more dangerous than other fuels, such as natural gas or gasoline, but its properties are unique and must be handled with appropriate care [33]. This is because it has the lowest molecular weight and the smallest molecule. These make hydrogen molecules more difficult to contain than the molecules of other gases. Moreover, it has the lowest density and therefore highest buoyancy of any element. These make hydrogen very easy to leak out from containers.

A hydrogen leak in itself is not a hazard, but it poses a potential fire hazard when it is mixed with air at appropriate concentrations. However, since hydrogen is colorless, odorless and tasteless, its presence cannot be detected by humans, and there may not be any warning signs before explosion results. The lower explosive limit of hydrogen-air mixtures lies at 4% hydrogen by volume [14]. In hydrogen based vehicles it is therefore important to monitor the hydrogen concentration inside the passenger compartment, inside the trunk and under the hood in the ambient air by means of a hydrogen sensor in case there is a leak.

1.3 Hydrogen Concentration

Since hydrogen can be so beneficial to the exhaust emissions, how much amount of hydrogen is involved as an additional fuel is turned out to be an important issue. There are two possible methods to supply the hydrogen on board a vehicle [36]. One method is to carry a hydrogen tank. It is very straightforward and the concentration of the hydrogen in the storage tank can get known when hydrogen is refilled. The disadvantage of this method is obvious that it is not very convenient because the hydrogen has to be refilled
from time to time. It is also not very safe when a hydrogen tank has to be carried on-board all the time.

As stated above, hydrogen is very easy to leak out from containers. Carrying a hydrogen tank is very dangerous. In that case, the hydrogen safety is a very serious concern. Thus, the other method, which is to generate hydrogen on-board by using the fuel in the fuel tank, can be a better choice. Hydrocarbons, e.g., diesel, can produce hydrogen through some chemical reactions such as steam reforming, water gas shift reaction and partial oxidation in a certain circumstance [6, 7, 8, 43, 45].

If the fuel from the fuel tank of the vehicle can be used to produce hydrogen, it will be much safer and much more convenient compared to bring a hydrogen tank on-board. But an on-board hydrogen generator has to be carried on the vehicle. Furthermore, the concentration of the hydrogen produced by the on-board generator is unknown. The amount of hydrogen generated can vary due to different water concentration in the exhaust, different temperature, different type of fuel and different amount of fuel [6, 7, 8, 9].

1.4 Hydrogen Sensors

From the above introduction, it is clear that for hydrogen safety diagnosis or for on-board hydrogen generation, a hydrogen sensor has to be used to detect hydrogen concentration. There are a lot of hydrogen sensor applications. Different applications may use different types of hydrogen sensors. Examples of hydrogen sensor applications are:

- Indoor or outdoor safety
- Industrial process monitoring
- Purity during manufacture and use
- Large scale (production / power) plants
- Feed streams in petrochemical industry
- Process control
- Safety in fuel cell automotive use
- In-line fuel monitoring for hydrogen feed

These applications all require highly reliable sensors, especially under harsh automotive conditions. Chemical sensors such as catalytic or metal-oxide semiconductor sensors, although very sensitive to hydrogen, have difficulties meeting the required robustness, such as immunity to poisons and low maintenance requirement \[46, 47, 48\].

### 1.5 Thesis Organization

In chapter 2, the potential hydrogen sensor automotive application will be introduced. It also reviews the currently commercialized hydrogen detecting mechanisms and sensors. Two comparisons are made: one was based on the literature and the other on the sensor manufacturer’s datasheets and application notes. The thermal conductivity sensors are selected and studied. The principles of thermal conductivity sensor and the thermal conductivity of hydrogen are also reviewed at the end of this chapter.

In chapter 3, how thermal conductivity of gas mixtures can be calculated is discussed. The Wassiljewa equation and the Mason-Saxena equation are introduced. How the simulation is setup by using these equations is described. 0% to 99.99% of hydrogen mixed with nitrogen is simulated. Up to 60% of hydrogen and up to 30% of carbon monoxide balanced in nitrogen are simulated. Different concentrations of
hydrogen and up to 20% of carbon dioxide balanced in nitrogen are also simulated. All the results are analyzed and summarized at the end of the chapter. The simulations are implemented in Matlab.

In chapter 4, experiments by using a commercially available thermal conductivity sensor is designed. The experiments are described in details. The detecting system and each functional module are explained. Experimental setups including hardware, gases, connection and operating procedures are also explained in details.

In chapter 5, the sensor has been tested in 5%, 10%, 30% and 99.99% of hydrogen in static condition and in different flow rates from 0 LPM ~ 7 LPM. It has also been tested in 10% hydrogen with 2%, 5% and 15% of carbon monoxide gas mixtures respectively. Different relative humidity from 37% to 78% has been tested. Zero drift of the sensor has also been explored. Experimental results are analyzed after each experiment.

In chapter 6, the conclusion of the thesis is presented in terms of the literature review, simulations and experimental results. Future work is also suggested. More investigations on different component gases, more experiments in different ambient conditions and more studies on potential application environments are recommended.
CHAPTER 2
LITERATURE REVIEW

2.1 Hydrogen Sensors in Automotive Applications

There are a lot of hydrogen sensors potentially applied in automotive industry. However, there is not a single sensor that meets all requirements for all applications, and no sensor is ideal for all applications. Requirements differ significantly. For hydrogen safety, sensors are typically calibrated to trigger warnings before the hydrogen concentration reaches the lower flammable limits (LFL) of hydrogen since the LFL of hydrogen is 4% (by volume) in air, e.g.: warnings at 5% of the LFL and 15% of the LFL and an alarm at 25% the LFL; these warning and alarm thresholds may represent a certain hydrogen concentrations like 0.2%, 0.6% and 1% in volume respectively. Then, the leak detection system indicates an alarm in order to activate protective measures before gas concentrations reach a dangerous level [33].

For the additional fuel use, if the hydrogen is generated through a hydrogen generator by using hydrocarbon fuel like diesel, the gas mixture generally contains nitrogen (N₂), hydrogen (H₂), oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO), water (H₂O) [56], sulfur compounds and some unburned hydrocarbons (HC) [10, 11, 12, 13]. Thus, the requirements of the hydrogen sensor are very different from the sensor used for hydrogen safety. The hydrogen sensor in the automotive exhaust application should at least have the following features:
➢ Be capable of working in a gas mixture including N₂, H₂, O₂, CO₂, CO, H₂O (vapor), hydrogen sulfide (H₂S) and some unburned HCs because the sensor has to be working in an exhaust gas environment.

➢ Have a hydrogen detection range potentially from 0% to 30% because 20% hydrogen was seen in researcher’s experiment [9].

➢ Be immune to poisons like H₂S because H₂S can damage sensors with catalyst using noble metals [15].

➢ Should require less maintenance due to the automotive application features.

➢ Should not have very big size due to the automotive application features.

2.2 Currently Commercialized Hydrogen Detecting Mechanisms and Sensors

There are various types of hydrogen sensors, which use different mechanisms to detect hydrogen, but not all sensors are commercialized. The most common and currently available sensor types are catalytic, electrochemical, metal-oxide semiconductor (MOx) and thermal conductivity as shown in Figure 2 [39].

![Image of commercialized H₂ sensor examples]

Figure 2: Currently commercialized H₂ sensor examples
2.2.1 Catalytic Sensors

A catalytic sensor detects hydrogen based on the temperature change which accompanies the exothermic oxidation reaction on a heated catalytic surface. It consists of two thin platinum wires each embedded in a ceramic bead (pellistor) and connected to each other in a Wheatstone bridge circuit as illustrated in Figure 2 [18, 19]. One pellistor is coated in a catalyst material which selectively catalyses the oxidation reaction of hydrogen, the surface of the other pellistor is inert. The pellistors are heated to 500°C – 550°C by passing a current through the circuit to promote the oxidation reaction. Hydrogen is oxidized on the bead surface and the heat of reaction causes an increase in temperature which changes the resistance of the platinum filament. This causes the Wheatstone bridge to be imbalanced and the measured imbalance of the bridge is linearly related to the hydrogen concentration [19].

![Figure 3: Schematic of a typical catalytic type combustible gas sensor [19]](image-url)
Catalytic sensors employ a well developed technology. However, they are not specific to hydrogen and responds to any combustible gas. Other chemical species, such as sulfur containing compounds (e.g.: H₂S), halogenated compounds and silicon containing compounds may cause a temporary or permanent loss of sensitivity to hydrogen [19].

2.2.2 Electrochemical Hydrogen Sensors

Electrochemical sensors generally consist of three electrodes, an electrolyte and a semi-permeable membrane which is selective to hydrogen diffusion, as depicted in Figure 4 [18, 19]. Hydrogen is oxidized at the surface of the sensing (working) electrode which consists of a catalyst, such as platinum; an oxidation reaction occurs at the counter electrode as illustrated in Figure 3. These reactions cause a potential difference between the electrodes and H₂ concentration is correlated with this potential difference by a non-linear relationship. A third reference electrode is added to the cell to improve repeatability and stability of measurements. The potentiostat provides a feedback control and assures that the voltage of the reference electrode is always close to zero regardless of the actual sensor current. The influence of polarization phenomena on the counter electrode is thus suppressed [19].

Electrochemical hydrogen sensors are commercially available and current research relates to electrode development [20], electrolyte development [21], improved sensitivity and faster response times [22]. Electrochemical sensors consume very little power during operation which is particularly convenient in automotive applications. Electrochemical sensors employing a liquid electrolyte cannot be operated or stored at low pressures or at sub-zero temperatures.
2.2.3 MOx Hydrogen Sensors

In metal-oxide semiconductor sensors, the active element of the sensor is an oxide layer, usually tin oxide, which has semi-conductive properties. The accepted detection mechanism [23] of this class of sensor is that, in the presence of reducing gases such as H₂ and CO, the gas particles diffuse into the sensing layer through pores and react with adsorbed oxygen on the semiconductor metal-oxide surface. This results in a decrease in the electrical resistance of the sensing layer.

Adsorption of hydrogen depends on the specific area, particle size and porosity of the metal-oxide material as well as the thickness of the sensing film [24]. An important
parameter in governing the sensitivity of metal-oxide sensor is the surface to volume ratio. Reduction of the metal-oxide grain size increases their sensitivity [25]. MOx sensors are small, easily mass produced and low-cost, nonetheless solid state metal-oxide sensors are reported to have numerous disadvantages including low selectivity and long response times [26].

2.2.4 Thermal Conductivity Sensors

Thermal conductivity sensors detect and measure between 0 and 100% by volume gases that have thermal conductivities significantly different to a reference gas [28], usually air as shown in Figure 5 [28]. Examples of these gases are: hydrogen, helium and methane. This also means that some gases such as oxygen, nitrogen and carbon monoxide cannot be measured practically as their thermal conductivities are too close to that of air [28].

![Figure 5: An example circuit of a thermal conductivity type H₂ sensor](image)

Reference element

Sensing element
Hydrogen gas has the highest thermal conductivity of all known gases [27]. Thermal conductivity sensors exploit this property for detection and monitoring of hydrogen. Thermal conductivity sensors consist of two identical elements. Any hydrogen concentration change in the target gas causes a change in the sensor temperature which changes the resistance of the element. Then, the concentration is indicated by the resistance change. Moreover, thermal conductivity hydrogen sensors do not require the presence of air/oxygen to operate [29]. They are also found to suffer less from long term drifts and are not prone to contamination from hydrogen sulfide like catalytic and MOx sensors [19].

2.3 Comparison of the Sensors

Two comparisons have been made: One is based on the general characteristics of the sensors; another on the datasheets and application notes of the commercialized sensors on the market. When comparisons are based on general characteristics, there are two factors to be considered: analytical and logistical:

- **Analytical**
  
  Selectivity, lower detection limit (LDL), analytical resolution, linear range (and dynamic range), response time, recovery time, repeatability, signal drift, effect of pressure, temperature, relative humidity.

- **Logistical**

  **Deployment parameters:**
  
  Cost, physical size, control circuitry, power requirement, electronic interface and maturity/availability

  **Operational parameters:**
Operational lifetime, consumables, calibration and maintenance requirements, sample size, matrix requirements, signal management

The general characteristics of electrochemical sensors summarized from the above review are listed in Table 1, and that of MOx sensors, thermal conductivity sensors and catalytic sensors are listed in Table 2, Table 3 and Table 4 respectively.

Table 1: General characteristics of electrochemical sensors

<table>
<thead>
<tr>
<th>Analytical</th>
<th>Logistical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good LDL</td>
<td>Commercially available</td>
</tr>
<tr>
<td>Good linearity</td>
<td>Low power</td>
</tr>
<tr>
<td>Poor to moderate repeatability (wide variation in results)</td>
<td>Moderate costs</td>
</tr>
<tr>
<td>Poor to moderate selectivity</td>
<td>Requires oxygen</td>
</tr>
<tr>
<td>Prone to environmental drift (e.g.: low temperature)</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>Prone to drift in high hydrogen</td>
<td>Moderate maintenance requirements</td>
</tr>
</tbody>
</table>

Table 2: General characteristics of MOX sensors

<table>
<thead>
<tr>
<th>Analytical</th>
<th>Logistical (headings everywhere)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate LDL</td>
<td>Mature commercial technology</td>
</tr>
<tr>
<td>Non-linear device</td>
<td>Low cost</td>
</tr>
<tr>
<td>Moderate to poor selectivity</td>
<td>High power</td>
</tr>
<tr>
<td>Poor to moderate repeatability</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>Slow response time, even slower recovery time</td>
<td>Oxygen is required</td>
</tr>
<tr>
<td>Prone to environmental drift (e.g.: temperature, relative humidity)</td>
<td>Moderate maintenance requirements</td>
</tr>
</tbody>
</table>
Table 3: General characteristics of thermal conductivity sensors

<table>
<thead>
<tr>
<th>Analytical</th>
<th>Logistical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good LDL</td>
<td>Commercially available</td>
</tr>
<tr>
<td>Good repeatability</td>
<td>Low power</td>
</tr>
<tr>
<td>Broad range available</td>
<td>Moderate costs</td>
</tr>
<tr>
<td>Moderate selectivity</td>
<td>Moderate maintenance requirements</td>
</tr>
<tr>
<td>Good response times</td>
<td></td>
</tr>
<tr>
<td>Prone to environmental drift (e.g.:</td>
<td></td>
</tr>
<tr>
<td>temperature, relative humidity)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: General characteristics of catalytic sensors

<table>
<thead>
<tr>
<th>Analytical</th>
<th>Logistical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good LDL</td>
<td>Commercially available</td>
</tr>
<tr>
<td>Good repeatability</td>
<td>High power</td>
</tr>
<tr>
<td>Poor selectivity</td>
<td>Moderate costs</td>
</tr>
<tr>
<td>Moderate response times</td>
<td>Oxygen is required</td>
</tr>
<tr>
<td>Low environmental drifts</td>
<td>Moderate maintenance requirements</td>
</tr>
</tbody>
</table>

From the above literature comparison, it can be seen that all the sensors have good LDL except MOx sensor which is moderate. Only does the electrochemical sensor have good linear region while others do not. The thermal conductivity sensor and catalytic sensor have good repeatability while others are poor to moderate. For selectivity, thermal conductivity sensor is rated moderate and others are rated poor or between poor to moderate. When comparison is based on the datasheets and application notes from hydrogen sensor manufacturers, the results become much clearer. The details are listed in Table 5.
Table 5: The comparison based on datasheets of commercially available sensors [16, 17, 34, 35]

<table>
<thead>
<tr>
<th>Types of sensors</th>
<th>Catalytic</th>
<th>Electrochemical</th>
<th>MOx</th>
<th>Thermal conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer of sensors</td>
<td>Kebaili</td>
<td>Honeywell</td>
<td>e2v</td>
<td>e2v</td>
</tr>
<tr>
<td>Model of sensors</td>
<td>KHS200</td>
<td>20525-0402</td>
<td>MICS-5315</td>
<td>VQ6</td>
</tr>
</tbody>
</table>
| Gas detecting | - Any combustible gas
  - Cross sensitivity
  - Poisoned by H₂S | - Cross sensitivity
  - Poisoned by H₂S
  - Wide variation | - Low accuracy
  - Long response and even longer recovery time | - Fast response time |
| Range | 0-4% | 0-4% | 0-4% | 0-100% |
| Other | - Need O₂ to operate | - Need O₂ to operate
  - Much maintenance | - Need O₂ to operate
  - Much maintenance | - Dependence on temperature |
| Main applications | - Fuel cell
  - H₂ storage
  - H₂ generation | - Fuel cell
  - Fuel tank
  - Automotive | - Fuel cell
  - Hydrogen storage | - Measuring Instrument
  - Oil industry |

2.4 Comparison Results

Hydrogen has not been widely used as an additional fuel on motor vehicles. Therefore, there is no hydrogen sensor which is especially developed to detect hydrogen concentration in this kind of application. However, for hydrogen safety applications, the detecting technologies are very common and mature. Hydrogen sensors used to detect hydrogen concentrations when hydrogen is used as an additional fuel are mainly discussed in this thesis.

From the literature and the existing commercialized hydrogen sensor datasheets comparisons, the thermal conductivity sensor is the most suitable for the application...
because it has board measurement range, it is not sensitive to carbon monoxide, it is immune to hydrogen sulfide and it has less maintenance. It is the closest one to the requirements which stated above in chapter 2.1.

2.5 Principles of Thermal Conductivity Sensors

Thermal conductivity sensors consist of two matched inert beads, which are similar to the compensators used in catalytic pellistor sensors. One bead is arranged to allow exposure to the target gas; the other bead is either sealed in a metal can (containing air) fitted to the header on which the beads are welded or sealed in a chamber within the certified head into which the sensor is eventually fitted [28, 57]. The sensors are typically connected in a simple Wheatstone bridge circuit and generally operated at a constant voltage.

When the beads are running in air, the beads loose heat at a similar rate, resulting in a set difference between the resistances and provide a signal to the bridge, which can be set to zero within the bridge circuit. When the sensor is exposed to the target gas, the atmosphere around the detecting element changes, resulting in a greater or lesser amount of heat being lost from the detector bead, leading to a drop or increase in the bead temperature and hence its resistance [49]. The drop or increase is dependent on the target gases thermal conductivity being greater than or less than the thermal conductivity of the reference gas. The reference bead being sealed does not show this effect. The drop or increase in the detecting bead resistance is shown by a negative or positive output of the sensor circuit [28].
Palladium (Pd) is used in many hydrogen sensors because it selectively absorbs hydrogen gas and forms the compound palladium hydride. Palladium sensors have to be protected against CO, sulfur dioxide and hydrogen sulfide [15, 16, 17]. CO is known to partially poison the permeation of H\(_2\) through Pd and its alloy membranes [30]. Resistance to CO is a critical requirement for the hydrogen sensor working in the automotive environment. The exhaust gas normally contains CO and the on-board hydrogen generator (if used) also produces large amount of CO while generating hydrogen by hydrocarbon fuel [9]. The CO concentration can reach as high as a half of the generated hydrogen concentration if steam reforming reaction takes place in the generator [9].

Since there is no catalytic process occurring in thermal conductivity sensors [44], the sensor does not poison in atmospheres containing poisons such as CO and H\(_2\)S; and since no catalytic processes are occurring, the sensor does not need oxygen to work [28]. Among the above four types of sensors, the thermal conductivity sensor is the only one which can be immune to CO, as well as H\(_2\)S.

### 2.6 Thermal Conductivity of Hydrogen

Hydrogen gas has the highest thermal conductivity of all known gases. Thermal conductivity sensors exploit this property for detecting hydrogen. The thermal conductivity relative to air of some gases is shown in Figure 6. It can be seen from Figure 6 that the thermal conductivity of hydrogen is 9.3 times as high as carbon dioxide and is seven times as high as nitrogen at 100 °C; the thermal conductivity values of nitrogen, oxygen and carbon monoxide are all very close at 100 °C. Hydrogen has the highest...
thermal conductivity and only helium is relatively close to it, but the thermal conductivity of helium is still around 22% less than that of hydrogen at 100 °C.

Figure 6: Gas relative thermal conductivity with temperature [28]
CHAPTER 3
SIMULATION RESULTS AND ANALYSIS

3.1 Hydrogen Detection by Thermal Conductivity Measurements

The detection of hydrogen in the gas mixtures mentioned in automotive applications by means of a thermal conductivity measurement is based on the large thermal conductivity difference between hydrogen and other component gases. The thermal conductivity of these gases is shown in Figure 6. Due to the dependency of the thermal conductivity on the gas temperature, the thermal conductivity of the hydrogen contained gas mixtures also depends on gas temperature as seen in Figure 6.

Therefore, the sole measurement of the thermal conductivity is not sufficient for a hydrogen sensor. The measured value must be corrected for its temperature dependence. Besides, the thermal conductivity sensor can only measure the thermal conductivity of the total target gas mixture. It cannot measure the hydrogen concentration directly. The hydrogen concentration has to be found out through some calculations.

3.2 Thermal Conductivity Calculation

The thermal conductivity of a gas mixture is not usually a linear function of its mole fraction [31]. Many techniques have been proposed such as Mason and Saxena modification [31]. All of them are essentially empirical and most of them reduce to some form of the Wassiljewa equation (equation 1) [31].

\[
\lambda_m = \sum_{i=0}^{n} \frac{y_i \lambda_i}{\Sigma_{j=1}^{n} y_j \lambda_j}
\]  

(1)
where,

\[ \lambda_m = \text{thermal conductivity of the gas mixture} \]

\[ \lambda_i = \text{thermal conductivity of component gas } i \]

\[ y_i, y_j = \text{mole fraction of components } i \text{ and } j \]

\[ A_{ij} = \text{a function, defined in equation } 2 \]

For non-polar gas mixtures, equation 1 is recommended with the Mason-Saxena relation (equation 2) [31] for \( A_{ij} \). Errors by using equation 2 are generally less than 3% to 4%. For non-polar/polar and polar/polar gas mixtures, none of the techniques examined are found to be particularly accurate. Thus, in such cases, errors from 5% to 8% may be expected when one employs the procedures recommended for non-polar gas mixtures.

\[ A_{ij} = \frac{\epsilon \left[ 1 + \left( \frac{\lambda_{tr i}}{\lambda_{tr j}} \right) \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2}{\left[ 8 \left( 1 + \frac{M_i}{M_j} \right)^{1/2} \right]} \]  

(2)

where,

\[ M = \text{molecular weight, g/mol} \]

\[ \lambda_{tr} = \text{monatomic value of the thermal conductivity} \]

\[ \epsilon = 1.065 \text{ numerical constant near unity for non-polar gases} \]

\[ \frac{\lambda_{tri}}{\lambda_{trj}} \text{ can be calculated by equation } 3. \]
\[ \frac{\lambda_{trl}}{\lambda_{trj}} = \frac{\Gamma}{\Gamma^i} \left[ \exp(0.0464T) - \exp(-0.2412T) \right] \]

where,

\( \Gamma \) defined in equation 4

\( T_r \) defined in equation 5

\[ \Gamma = 210 \left( \frac{T_c M^2}{P_c^4} \right)^{1/6} \]

where,

\( M \) = molecular weight, g/mol

\( T_c \) = critical temperature, K

\( P_c \) = critical pressure, bar

\[ T_r = T/T_c \]

where,

\( T_c \) = critical temperature, K

\( T \) = gas temperature, K
Table 6: Basic constants used for calculation at 26.7 °C [31,32]

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature</td>
<td>32.98</td>
<td>126.20</td>
<td>304.12</td>
<td>132.85</td>
</tr>
<tr>
<td>(Tₑ, K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical temperature</td>
<td>12.93</td>
<td>33.98</td>
<td>73.74</td>
<td>34.94</td>
</tr>
<tr>
<td>(Pₑ, bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2.016</td>
<td>28.014</td>
<td>44.01</td>
<td>28.010</td>
</tr>
<tr>
<td>(g/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.1870</td>
<td>0.0261</td>
<td>0.0166</td>
<td>0.0251</td>
</tr>
<tr>
<td>(W/(m·K))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3 Simplifications

From equation 1, it can be seen that in order to calculate the thermal conductivity of the gas mixture, all the mole fractions of the component gases have to be known which is unlikely to be possible. The exhaust gas is the most complicated gas mixture in automotive applications. When the particulate matters, liquid unburned hydrocarbons and water are filtered out, N₂, H₂, O₂, CO₂, CO and some unburned hydrocarbons are the dominant gases in the gas mixture. Therefore, N₂, H₂, O₂, CO₂, CO and some unburned hydrocarbons are assumed to be contained in the target gas mixture in this thesis. In Table 7 below, the thermal conductivity values of all the gases in the assumption have been listed. The thermal conductivity values of these gases at 26.7 °C have been plotted in Figure 7.
Table 7: Examples of gas thermal conductivities at various temperatures [32]

<table>
<thead>
<tr>
<th></th>
<th>Thermal conductivity at 4.4 °C (W/(m·K))</th>
<th>Thermal conductivity at 26.7 °C (W/(m·K))</th>
<th>Thermal conductivity at 48.9 °C (W/(m·K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.024</td>
<td>0.026</td>
<td>0.028</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.023</td>
<td>0.025</td>
<td>0.027</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.024</td>
<td>0.026</td>
<td>0.028</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.025</td>
<td>0.027</td>
<td>0.029</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.175</td>
<td>0.187</td>
<td>0.197</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.015</td>
<td>0.017</td>
<td>0.018</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.014</td>
<td>0.016</td>
<td>0.018</td>
</tr>
<tr>
<td>i-Butane</td>
<td>0.014</td>
<td>0.016</td>
<td>0.019</td>
</tr>
<tr>
<td>n-Propane</td>
<td>0.016</td>
<td>0.018</td>
<td>0.020</td>
</tr>
<tr>
<td>Water vapor</td>
<td>0.016</td>
<td>0.018</td>
<td>0.020</td>
</tr>
</tbody>
</table>

As it is shown in Figure 7, all the gases have been divided into three groups by their thermal conductivity values:

- The thermal conductivity values of CO, N\textsubscript{2}, O\textsubscript{2} are very close, so they are grouped together;
- The thermal conductivity values of CO\textsubscript{2}, water vapor and some HC vapors are much lower than the CO, N\textsubscript{2}, O\textsubscript{2} group, but they themselves are very close, so they form a group;
- The H\textsubscript{2} is so different that it is located at the top. So H\textsubscript{2} forms a group by itself alone.
Therefore, it can be approximated that the thermal conductivity of the target gas mixture equals the thermal conductivity of the three-gas-mixture of \( \text{N}_2 \), \( \text{H}_2 \) and \( \text{CO}_2 \). Of course, this will introduce some errors into the total measurement accuracy but not many.

### 3.4 Simulation Setup

The Wassiljewa equation (equation 1) and the Mason-Saxena equation (equation 2) [31] were used in the simulation to show how the thermal conductivity of the gas mixture would change when different concentrations of different gases were mixed together. Equations 3 ~ 5 were involved in the calculation of equation 2. Component gas
species, mole fractions of each gas and gas mixture temperature could all be modified. Gas pressure was assumed to be within $10^{-3}$ bar to 10 bar because the Wassiljewa equation was appropriate for this pressure region. The thermal conductivity increases about 1% or less per bar [31], so the gas pressure was not set to be modified in the simulation.

All the constant values in the equations could be retrieved from Table 6. The simulation inputs and conditions were set and defined in subsection 3.5 and its subsections. The output were stored in files and plotted into figures. All the simulations were implemented in Matlab.

3.5 Calculated Results

Thermal conductivity of a two-gas mixture, which was hydrogen and nitrogen gas mixture, has been calculated in this section. The thermal conductivity of a three-gas mixture, the hydrogen, carbon monoxide and nitrogen, was also calculated. All the calculations and simulations were completed in Matlab. A comparison was made between them. The results are analyzed below.

3.5.1 Calculated Results-H$_2$ and N$_2$ Gas Mixture

The purpose of this calculation is to see that the thermal conductivity of the gas mixture also changes accordingly when H$_2$ concentration varies. This is the baseline requirement of the sensor. If there is no thermal conductivity change on the gas mixture, nothing can be measured. Equation 1 can be expanded as equation 6 to calculate the thermal conductivity of the two-gas gas mixture.

$$\lambda_m = \frac{y_1\lambda_1}{y_1 + y_2\lambda_{12}} + \frac{y_2\lambda_2}{y_1\lambda_{21} + y_2}$$  (6)
The simulation conditions in this simulation were: 300 K in temperature, 1 atm (atmospheric pressure) in pressure and 0% ~ 99.99% of hydrogen concentrations. Equation 3 was used. The numbers in Table 8 below are some thermal conductivity values from the calculation. The total calculated results of hydrogen sweeping from 0% to 99.99% are plotted in the Figure 8 below. From this calculation, it can be seen that as the H₂ concentration increases, the thermal conductivity (TC) of the gas mixture also increases.

Table 8: Calculated results of H₂ and N₂ mixture at 300 K

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>W/(m·K)</td>
<td>0.0307</td>
<td>0.0355</td>
<td>0.0573</td>
<td>0.1870</td>
</tr>
</tbody>
</table>

Figure 8: Calculation of H₂ and N₂ mixture at 300 K
3.5.2 Calculated Results-H$_2$, CO and N$_2$ Gas Mixture

The purpose of this simulation is to investigate the thermal conductivity change when CO is added to the H$_2$ and N$_2$ gas mixture. At the same time, it is to see if it is feasible to approximate CO and N$_2$ gas mixture as N$_2$ gas only from the thermal conductivity point of view.

Equation 1 can be expanded as equation 7 to calculate the thermal conductivity of the three-gas gas mixture. $y_1$ is the molar fraction of H$_2$; $y_2$ is the molar fraction of N$_2$ and $y_3$ is the molar fraction of CO. If substituting $y_2$ in equation 7 by equation 8, equation 7 can be rewrite as equation 9.

\[
\lambda_m = \frac{y_1\lambda_1}{y_1+y_2A_{12}+y_3A_{13}} + \frac{y_2\lambda_2}{y_1A_{21}+y_2+y_3A_{23}} + \frac{y_3\lambda_3}{y_1A_{31}+y_2A_{32}+y_3}
\]  

(7)

\[
y_2 = 1 - y_1 - y_3
\]  

(8)

\[
\lambda_m = \frac{y_1\lambda_1}{y_1+(1-y_1-y_3)A_{12}+y_3A_{13}} + \frac{(1-y_1-y_3)\lambda_2}{y_1A_{21}+(1-y_1-y_3)+y_3A_{23}} + \frac{y_3\lambda_3}{y_1A_{31}+(1-y_1-y_3)A_{32}+y_3}
\]  

(9)

This simulation was to show the steam reforming in the on-board generator. The carbon monoxide concentration was set to a half of the hydrogen concentration in volume, that is, [CO] = [H$_2$]/2. The simulation conditions were 300 K in temperature, 1 atm in pressure, and equation 9 was used. Here “[CO]” means percentage of CO; “[H$_2$]” means percentage of H$_2$.

The numbers in Table 9 below are some thermal conductivity values from the calculation. The total calculated results of hydrogen sweeping from 0% to 60% are
plotted in the following Figure 9. From the calculation, it can be seen that as the H₂ and CO concentrations increase, the thermal conductivity of the gas mixture increases.

### Table 9: Calculated results of H₂, CO and N₂ mixture at 300 K

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>5%[H₂]</th>
<th>10%[H₂]</th>
<th>30%[H₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%[CO]</td>
<td>5%[CO]</td>
<td>15%[CO]</td>
<td></td>
</tr>
<tr>
<td>W/(m·K)</td>
<td>0.0306</td>
<td>0.0353</td>
<td>0.0566</td>
</tr>
</tbody>
</table>

Figure 9: Calculations of H₂, CO and N₂ mixture at 300 K
3.5.3 Calculated Results- H₂, CO and N₂ Gas Mixture vs. H₂ and N₂ Gas Mixture

The purpose of this calculation was to combine the previous two plots into one plot, in order to compare if there is any difference between [H₂ + CO + N₂] gas mixture and [H₂+ N₂] gas mixture. Furthermore, it is also to discover if it is feasible to approximate [CO + N₂] mixture as N₂ gas only from the thermal conductivity point of view. The simulation conditions in this calculation were:

- [H₂ + N₂], hydrogen concentration sweeping from 0%~99.99%
- [CO]=[H₂]/2, hydrogen concentration sweeping from 0%~60%
- Balance gas: N₂
- Temperature: 300 K
- Pressure: 1 atm
- Equation used: Equation 7 was used for the two-gas mixture and equation 9 was used for the three-gas mixture.

Table 10: [H₂ + CO + N₂] vs. [H₂ + N₂] at 300 K

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>5% [H₂]</th>
<th>10% [H₂]</th>
<th>30% [H₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/(m·K)</td>
<td>0.0307</td>
<td>0.0355</td>
<td>0.0573</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>5% [H₂]</th>
<th>10% [H₂]</th>
<th>30% [H₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas mixture</td>
<td>2.5% [CO]</td>
<td>5% [CO]</td>
<td>15% [CO]</td>
</tr>
<tr>
<td>W/(m·K)</td>
<td>0.0306</td>
<td>0.0353</td>
<td>0.0566</td>
</tr>
</tbody>
</table>

The numbers in Table 10 above are some thermal conductivity values from the calculation. The total calculated results, which hydrogen swept from 0% to 60% and CO
from 0% to 30%, together with hydrogen from 0% to 99.99%, are plotted in Figure 10 below. From the calculation, it can be seen that as the H\textsubscript{2} and CO concentrations increase, the thermal conductivity of the gas mixture increases.

From the calculation and comparison results, it can be seen that it is valid to assume that the thermal conductivity of [H\textsubscript{2} + CO + N\textsubscript{2}] gas mixture is equal to the thermal conductivity of [H\textsubscript{2} + N\textsubscript{2}] gas mixture. The two results show very similar thermal conductivity values and the two curves in Figure 10 almost overlap.

![Figure 10: [H\textsubscript{2} + CO + N\textsubscript{2}] vs. [H\textsubscript{2} + N\textsubscript{2}] gas mixture at 300 K](image)

- Temperature: 300 K
- Solid line: [H\textsubscript{2} + N\textsubscript{2}]
- Dotted line: [H\textsubscript{2} + CO + N\textsubscript{2}]
3.5.4 Calculated Results-10% H₂ and (0%~90%) CO in N₂ Gas Mixture

The purpose of this simulation is to see if there is any influence on the thermal conductivity of the gas mixture when the CO concentration changes. The simulation conditions were:

- H₂ concentration: 10% constantly
- CO concentration: sweeping from 0% to 90%.
- Balance gas: N₂
- Temperature: 300 K
- Pressure: 1 atm
- Equation used: Equation 9

Table 11: Calculated results-10% H₂ and (0%~90%) CO in N₂

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>W/(m·K)</td>
<td>0.0353</td>
<td>0.0351</td>
<td>0.0347</td>
<td>0.0345</td>
<td>0.0341</td>
</tr>
</tbody>
</table>

The numbers in Table 11 above provide some thermal conductivity values from the calculation. The total calculated results of sweeping CO from 0% to 90% plus 10% H₂ is plotted in the Figure 11. From this calculation, it can be seen that as the CO concentration increases, the thermal conductivity of the gas mixture is not sensitive to the change.
3.5.5 Calculated Results-H₂ vs. CO₂

The purpose of this simulation is to see if there is any influence on the thermal conductivity of [H₂ + N₂] gas mixture when CO₂ is added. Simulation conditions in this calculation were:

- Make the thermal conductivity of the gas mixture equal to 0.0307 W/(m·K) which is the thermal conductivity of 5% of H₂ in N₂.
- Sweep CO₂ from 0% to 20%
- Balance gas: N₂
- Temperature: 300 K
- Pressure: 1 atm
Equation used: Equation 9

The numbers in Table 12 below provide some thermal conductivity values from the calculation. The total calculated result of carbon dioxide sweeping from 0% to 20% is plotted in Figure 12 below. From this calculation, it can be seen that:

a) When the concentration of CO\(_2\) increases, the concentration of H\(_2\) has to increase to balance it to maintain the thermal conductivity of the gas mixture.

b) For every 1% increase of CO\(_2\), there is less than a 0.2% increase in H\(_2\).

c) The percentage increase of H\(_2\) is not linear.

![Figure 12: Calculation results of H\(_2\) vs. CO\(_2\)](image-url)
Table 12: Calculation results of H₂ vs. CO₂

<table>
<thead>
<tr>
<th>H₂</th>
<th>5.0%</th>
<th>5.2%</th>
<th>5.4%</th>
<th>5.6%</th>
<th>5.8%</th>
<th>6.0%</th>
<th>6.2%</th>
<th>6.3%</th>
<th>6.5%</th>
<th>6.7%</th>
<th>6.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0%</td>
<td>1%</td>
<td>2%</td>
<td>3%</td>
<td>4%</td>
<td>5%</td>
<td>6%</td>
<td>7%</td>
<td>8%</td>
<td>9%</td>
<td>10%</td>
</tr>
<tr>
<td>H₂</td>
<td>7.1%</td>
<td>7.2%</td>
<td>7.4%</td>
<td>7.6%</td>
<td>7.8%</td>
<td>7.9%</td>
<td>8.1%</td>
<td>8.3%</td>
<td>8.5%</td>
<td>8.6%</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>11%</td>
<td>12%</td>
<td>13%</td>
<td>14%</td>
<td>15%</td>
<td>16%</td>
<td>17%</td>
<td>18%</td>
<td>19%</td>
<td>20%</td>
<td></td>
</tr>
</tbody>
</table>

3.6 Analysis of the Calculated Results

From the above calculations, it can be seen that:

a) In hydrogen and nitrogen gas mixture, as the H₂ concentration increases, the thermal conductivity of the gas mixture increases. If a sensor can detect the thermal conductivity change by some resolution which the application requires, this means that the gas thermal conductivity can be measured.

b) In hydrogen, nitrogen and carbon monoxide gas mixture, as the H₂ and CO concentrations increase, the thermal conductivity of the gas mixture increases.

c) When comparing the thermal conductivity of H₂ and N₂ gas mixture and the thermal conductivity of H₂, CO and N₂ gas mixture, the two curves almost overlap. In other words, it means that if there is CO or there is no CO presented in the gas mixture, the thermal conductivity of the gas mixture is not sensitive to it.

d) In H₂, CO and N₂ gas mixture, as the CO concentration increases, the thermal conductivity of the gas mixture does not change.

e) In H₂, CO₂ and N₂ gas mixture gas mixture, the thermal conductivity of the mixture is kept constant. When concentration of CO₂ increases, the concentration of H₂ has to increase to balance it and to maintain the thermal conductivity of the
gas mixture unchanged. For every 1% increase of CO₂, there is a less than 0.2% of increase on H₂ (The increase of H₂ is not linear). For 10% CO₂, 1.9%H₂ is required to balance the CO₂; for 20% CO₂, 3.6% H₂ is required. In real application, if the CO₂ concentration is not accurate, the effect on H₂ concentration calculation is not huge. For 20% error on CO₂ concentration, the max error on H₂ is 3.6%. 
CHAPTER 4
EXPERIMENTS DESIGN

4.1 Purpose of the Experiments
The main purpose of the experiments was to compare the calculated results and the experimental results, to see if the thermal conductivity sensor (TCS) has the ability to detect the hydrogen concentration in the proposed application:

a) If the TCS can distinguish different concentrations of H₂ in N₂;
b) If the TCS can distinguish different concentrations of H₂ in N₂, or H₂ and CO in N₂ gas mixture; and at the same time, if the addition of CO has any influence on the experimental result when compared with the H₂ and N₂ gas mixture;
c) How the TCS responds to different flow rates and what is the difference between gas flows and static conditions;
d) How the TCS responds to different relative humidity (RH);
e) How the TCS responds when temperature changes.

4.2 Description of the Experiments
Five experiments were done, and they are described in Table 13. The response time of the sensor has not been tested in this research because different sensor manufacturers use different processes. The response time varies. It is reported that the response time produced by some vendors can be one second [39].
Table 13: Descriptions of experiments

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Gas mixture</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>H₂ in N₂ (static condition)</td>
<td>To see if the sensor can distinguish different concentrations of H₂ in N₂</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>H₂ and CO in N₂ (static condition)</td>
<td>To see that if CO has no influence on hydrogen detection by TCS; if TCS can distinguish different concentrations of H₂ in CO and N₂ gas mixture</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>H₂ in N₂ in gas flows</td>
<td>To see if the TC sensor can distinguish different concentrations of H₂ in various gas flows</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>In air but RH and temperature varies</td>
<td>To see how the sensor is working under different RH and temperatures</td>
</tr>
<tr>
<td>Experiment 5</td>
<td>In air</td>
<td>To see if there is any zero drift (test under room temperature, 1 atm and 32% RH)</td>
</tr>
</tbody>
</table>

Comments:

*All the experiments, except experiment 4, were done under room temperature and 1 atm; experiment 4 was done under 1 atm and various temperatures and relative humidities.

**Bottled gases were used and all the concentrations of the component gases were known.

***For hydrogen safety, the applications are very mature so only the hydrogen in a gas mixture environment was tested by the experiments.

### 4.3 System Design for the Experiments

The following devices were used in the detecting system: a thermal conductivity sensor, a temperature sensor, a micro-controller unit (MCU), an analog to digital converter (ADC) and some serial interface. The detecting system mainly consists of three
functional modules: one detection module, one control module and one interface module.

See the block diagram in Figure 13.

Figure 13: Block diagram of the detecting system

Comments:

* The “red dotted line” means optional.
** The “blue dotted line blocks” are functional modules.
*** For the interfaces, it can be either one or more, or all, e.g.: USB or RS232 or both.

4.3.1 Detection Module

This module is to detect the hydrogen, the temperature and the pressure (if necessary) in the target gas flow. When there is a concentration change (assume the temperature and the pressure are unchanged), there will be a voltage change at the output of the sensor accordingly.
➢ The thermal conductivity sensor: Detecting the thermal conductivity of the gas mixture. It always gives a voltage output after being powered on. If the gas thermal conductivity changes, the output voltage also changes.

➢ The temperature sensor: The thermal conductivity of a gas can vary with temperature, so a temperature sensor is necessary. The temperature sensor is to provide the temperature of the target gas flow continuously. In the real use of the TCS, it is not easy or even not possible to calibrate the sensor under all the possible temperatures. To keep the gas temperature constant is a better solution. In the experiments, the temperatures are kept unchanged.

➢ The pressure sensor (if used): It provides the pressure of the gas flow continuously. This sensor can be optional because the effect is very little (less than 1%/bar) if the pressure change is within 0.001 bars to 10 bar [31]. The pressure sensor was not used in the experiments because all the experiments were done at a constant pressure of 1 atmosphere.

4.3.2 Interface Module

This module is to communicate with other controllers or PCs. In the experiments, all the sampled signals were converted to digital signals by the ADC and then processed by the controller. After that, the assembled data was transmitted to the PC through a USB interface and saved on a hard disc. If the sensor is used on a vehicle, it is better to use CANBus; if the sensor is used indoors, RS232, RS485, USB are all good options to be used. USB was selected in the experiments.
4.3.3 Control Module

This module is to sample and to calculate the hydrogen concentration at each sampling time. When doing the sampling, a voltage from the TCS, a temperature from the temperature sensor and a pressure from the pressure sensor (if a pressure sensor is used) can be read. The voltages are then converted by an ADC to digital signals and processed by the MCU. The hydrogen concentration is calculated by those values. The ADC used is a 16-bit ADC. The supply voltage is 3.3V and the reference voltage is also 3.3V. The resolution is 0.05 mV calculated in equation 10.

\[ 3.3V / 2^{16} = 3.3V / 65536 = 5 \times 10^{-5} V = 0.05 \text{ mV} \quad (10) \]

4.4 Experimental Setups

There are five different experiments each of which has a different purpose, so the setup may be different. Therefore, three different setups were used in the experiments. The following assumptions were made:

a) There is no condensation (e.g.: no water);

b) The concentrations of all the gases and temperature of the gas mixture remains constant until a value has been read from the sensor;

c) The reference gas in the TCS is N$_2$ instead of air which is the actual reference sealed in the reference element. The thermal conductivity of N$_2$ and air are almost the same. Thermal conductivity of air is 62.2 and thermal conductivity of N$_2$ is 62.4 (unit: cal/sec cm °C x 10$^6$) at 26.7°C. The ratio between N$_2$ and air is 62.4/62.2 =1.003;

d) Pressure change is ignored. (The pressure change is within 5 psig in all the experiments);
e) In all the experiments (except experiment 4), constant temperature is assumed during the entire process for the purpose of simplifying the calculation.

4.4.1 Experimental Setup 1

➢ Setup 1–hardware:

<table>
<thead>
<tr>
<th>System requirement</th>
<th>Experiment use</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A thermal conductivity sensor</td>
<td>VQ600m/3 sensing head</td>
<td>e2v</td>
</tr>
<tr>
<td>A temperature sensor</td>
<td>LM60</td>
<td>National semiconductor</td>
</tr>
<tr>
<td>Micro-controller</td>
<td>MSP430F2616</td>
<td>TI</td>
</tr>
<tr>
<td>ADC</td>
<td>AD7689</td>
<td>Linear tech</td>
</tr>
<tr>
<td>RS232</td>
<td>MSP430F2616</td>
<td></td>
</tr>
<tr>
<td>Solenoid</td>
<td>SV125 0-200 psi</td>
<td>Omega</td>
</tr>
<tr>
<td>Regulator</td>
<td>3000 psi inlet 2-50 psi outlet</td>
<td>Omega</td>
</tr>
<tr>
<td>Gauge</td>
<td>0-60 psi</td>
<td>Omega</td>
</tr>
<tr>
<td>Tubing</td>
<td>175 psi</td>
<td>Omega</td>
</tr>
<tr>
<td>Flow cap</td>
<td>DAS546633AA</td>
<td>e2v</td>
</tr>
</tbody>
</table>
➢ Setup 1–gases

Table 15: Setup 1–gases

<table>
<thead>
<tr>
<th>Gases diluted in N\textsubscript{2}</th>
<th>Supplier</th>
<th>Supply Pressure range (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H\textsubscript{2}]-5%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
<tr>
<td>[H\textsubscript{2}]-10%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
<tr>
<td>[H\textsubscript{2}]-30%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
<tr>
<td>[H\textsubscript{2}]-99.99%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
<tr>
<td>[H\textsubscript{2}]-10%, [CO]-2%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
<tr>
<td>[H\textsubscript{2}]-10%, [CO]-5%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
<tr>
<td>[H\textsubscript{2}]-10%, [CO]-15%</td>
<td>Praxair</td>
<td>3~6</td>
</tr>
</tbody>
</table>

➢ Setup 1–connections

Figure 14: Setup 1–connections
4.4.2 Experimental Setup 2

Setup 2–hardware

The main hardware difference between setup 1 and setup 2 is that a flow meter is added between the gas cylinder and the sensor inlet as shown in Figure 15. The gas flow rate can be adjusted during the experiment.

Figure 15: Flow meter in the setup
### Table 16: Setup 2–hardware

<table>
<thead>
<tr>
<th>System requirement</th>
<th>Experiment use</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A thermal conductivity sensor</td>
<td>VQ600m/3 sensing head</td>
<td>e2v</td>
</tr>
<tr>
<td>A temperature sensor</td>
<td>LM60</td>
<td>National semiconductor</td>
</tr>
<tr>
<td>Micro-controller</td>
<td>MSP430F2616</td>
<td>TI</td>
</tr>
<tr>
<td>ADC</td>
<td>AD7689</td>
<td>Linear tech</td>
</tr>
<tr>
<td>USB</td>
<td>CP2012</td>
<td>Silicon lab</td>
</tr>
<tr>
<td>Solenoid</td>
<td>SV125 0-200 psi</td>
<td>Omega</td>
</tr>
<tr>
<td></td>
<td>Response time: 4-15 ms</td>
<td></td>
</tr>
<tr>
<td>Regulator</td>
<td>3000 psi inlet 2-50 psi outlet</td>
<td>Omega</td>
</tr>
<tr>
<td>Gauge</td>
<td>0-60 psi</td>
<td>Omega</td>
</tr>
<tr>
<td>Tubing</td>
<td>175 psi</td>
<td>Omega</td>
</tr>
<tr>
<td>Flow cap</td>
<td>DAS546633AA</td>
<td>e2v</td>
</tr>
<tr>
<td></td>
<td>(Average sectional area: 4 cm²)</td>
<td></td>
</tr>
<tr>
<td>Flow meter</td>
<td>Range: 0-7 LPM (liter per minute)</td>
<td>Cole parmer</td>
</tr>
<tr>
<td></td>
<td>Error: 10%</td>
<td></td>
</tr>
</tbody>
</table>

➢ Setup 2–gases

### Table 17: Setup 2–gases

<table>
<thead>
<tr>
<th>Gases diluted in N₂</th>
<th>supplier</th>
<th>Supplied pressure range (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₂]-5%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
<tr>
<td>[H₂]-10%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
<tr>
<td>[H₂]-30%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
<tr>
<td>[H₂]-99.99%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
<tr>
<td>[H₂]-10%, [CO]-2%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
<tr>
<td>[H₂]-10%, [CO]-5%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
<tr>
<td>[H₂]-10%, [CO]-15%</td>
<td>Praxair</td>
<td>3~8</td>
</tr>
</tbody>
</table>
4.4.3 Experimental Setup 3

Table 18: Setup 3–hardware

<table>
<thead>
<tr>
<th>System requirement</th>
<th>Experiment use</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A thermal conductivity sensor</td>
<td>VQ600m/3 sensing head</td>
<td>e2v</td>
</tr>
<tr>
<td>A temperature sensor</td>
<td>LM60</td>
<td>National semiconductor</td>
</tr>
<tr>
<td>Micro-controller</td>
<td>MSP430F2616</td>
<td>TI</td>
</tr>
<tr>
<td>ADC</td>
<td>AD7689</td>
<td>Linear tech</td>
</tr>
<tr>
<td>USB</td>
<td>CP2012</td>
<td>Silicon lab</td>
</tr>
<tr>
<td>Flow cap</td>
<td>DAS546633AA</td>
<td>e2v</td>
</tr>
<tr>
<td>(Average sectional area: 4 cm²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermometer</td>
<td></td>
<td>Accu temp</td>
</tr>
<tr>
<td>Humidity meter</td>
<td></td>
<td>Accu temp</td>
</tr>
</tbody>
</table>
4.5 Steps of Operation

- Procedure 1 - Static

When the sensor was tested in static conditions and in flows, different experimental setups were used. The operation procedures were also different. When the sensor was tested in a static gas mixture during the experiments, the operation procedure in Figure 17 was followed. When the sensor was tested in a gas flow during the experiments, the operation procedure in Figure 18 was followed.
Procedure 2 - Gas flow

Figure 18: Steps of operation—gas flow
5.1 Results and Analysis of Experiment 1-Tested in Static [H₂+ N₂] Gases

In order to see if the sensor can distinguish different concentrations of H₂ in N₂, the gases in a static condition were tested in this experiment. Different concentrations of H₂ (diluted in nitrogen) have been tested (5%, 10%, 30% and 99.99% of H₂). Experimental setup 1 and operational procedure 1 were used.

- **Tested in 5% hydrogen**

  When the target gas was 5% hydrogen, the output voltage of TCS kept going down rapidly until the 34th second at which, it reached a maximum of -25.42 mV and then kept relatively stable, as it is shown in Figure 19. This relative stable condition could stay as long as the concentration remained the same. It had kept stable for 118 seconds as seen in Figure 19.

![Figure 19: Experimental outputs–5% H₂](image-url)
> **Tested in 10% hydrogen**

When the target gas was 10% hydrogen, the output voltage of the thermal conductivity sensor (TCS) kept going down rapidly until the 24th second; the curve was getting flat and kept relatively stable from this point. A “-54.86 mV” was read from the output as it is shown in Figure 20. This relative stable condition had stayed for 156 seconds as seen in Figure 20.

![Figure 20: Experimental outputs–10% H₂](image)

> **Tested in 30% hydrogen**

When the target gas was 30% hydrogen, the output voltage of TCS dropped down even more rapidly until the 19th second; the curve was getting flat and kept relatively stable from this point. A “-152.9 mV” was read from the output, as it is shown in Figure 21. This relative stable condition had stayed for 245 seconds.
Figure 21: Experimental outputs–30% H₂

- Tested in 99.99% hydrogen

When the target gas was 99.99% hydrogen, the output voltage of TCS dropped down very fast until the 14th second; the curve was getting flat and kept relatively stable from this point. A “−351.44 mV” was read from the output, as it is shown in Figure 22. This relative stable condition had stayed for 356 seconds.

Figure 22: Experimental outputs–99.99% H₂
The experimental result and analysis of experiment 1

The experimental result of this experiment is in Table 19. The sampling time was 10 seconds after the stable point. To make it more convenient, the “measured value” in this table was the absolute value of the output reading. The results were also plotted in Figure 23.

Table 19: Results of experiment 1

<table>
<thead>
<tr>
<th>Experiment1 at 24°C±3°C:</th>
<th>5%[H₂]</th>
<th>10%[H₂]</th>
<th>30%[H₂]</th>
<th>99.99%[H₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured value</td>
<td>25.82 mV</td>
<td>56.12 mV</td>
<td>153.84 mV</td>
<td>364.94 mV</td>
</tr>
</tbody>
</table>

Figure 23: Results of experiment 1
From Figure 23 and Figure 8, it can be seen that the trends of these two curves are very similar. But the values in these two figures have different units. In order to put these two curves into one plot, equation 11 and 12 were used to remove the units of the experimental results and the calculated results.

\[ V_{ur,mea} = \frac{V_{mea}}{\text{mean}(V_{S,MEA})} \]  \hspace{1cm} (11)

where

- \( V_{ur,mea} \) = the unit-removed value of the measured value
- \( V_{mea} \) = the measured value
- \( V_{S,MEA} \) = a set of measured values

Or

\[ V_{ur,cal} = \frac{V_{cal}}{\text{mean}(V_{S,CAL})} \]  \hspace{1cm} (12)

where

- \( V_{ur,cal} \) = unit removed value of calculated value
- \( V_{cal} \) = calculated value
- \( V_{S,CAL} \) = a set of calculated values

The calculated results of the unit-removed values of experiment 1 by using equation 11 and equation 12 are shown in Table 20. To make it clearer, the calculated values and experimental values were put into one plot in Figure 24. When comparing the
experimental result with the calculated result, the trend is very similar, and the values are also very close. It is the same as the simulation results that the gas mixture thermal conductivity changes as the gas concentration changes. The change can be detected and measured by the thermal conductivity sensor. Moreover, once the sensor output became stable, it stayed stable as long as the concentration remained the same. This feature is very good for sampling.

Table 20: Calculated results of the unit-removed values of experiment 1

<table>
<thead>
<tr>
<th>Experiment1</th>
<th>5% H₂</th>
<th>10% H₂</th>
<th>30% H₂</th>
<th>99.99% H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated value W/(m·K)</td>
<td>0.0307</td>
<td>0.0355</td>
<td>0.0573</td>
<td>0.1870</td>
</tr>
<tr>
<td>Measured value</td>
<td>25.82 mV</td>
<td>56.12 mV</td>
<td>153.84 mV</td>
<td>364.94 mV</td>
</tr>
<tr>
<td>( V_{ur_mea} )</td>
<td>0.17</td>
<td>0.37</td>
<td>1.02</td>
<td>2.43</td>
</tr>
<tr>
<td>( V_{ur_cal} )</td>
<td>0.40</td>
<td>0.46</td>
<td>0.74</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Figure 24: The calculated values vs. experimental values of experiment 1
5.2 Results and Analysis of Experiment 2-Tested in Static [H₂+CO+N₂] Gases

In order to see that CO has no influence on hydrogen detection by TCS, different concentrations of H₂+CO (diluted in nitrogen) gas mixtures have been tested (10% H₂ and 2% CO, 10% H₂ and 5% CO and 10% H₂ and 15% CO). This experiment also can see if TCS can distinguish different concentrations of H₂ in CO and N₂ gas mixture. Experimental setup 1 and operational procedure 1 were used in this experiment.

➢ **Tested in 10% H₂ and 2% CO**

When the target gas was 10% hydrogen and 2% carbon monoxide mixture, the output voltage of TCS kept going down rapidly until the 18th second (started from the 9th second); it reached a voltage of -58.08 mV and then kept relatively stable, as shown in Figure 25.

![Figure 25: Experimental outputs in 10% H₂ and 2% CO](image-url)
- **Tested in 10% hydrogen and 5% carbon monoxide**

  When the target gas was 10% hydrogen and 5% carbon monoxide mixture, the output voltage of TCS kept going down rapidly until the 19th second; it reached a voltage of -59.53 mV and then kept relatively stable, as shown in Figure 26.

![Graph showing experimental outputs in 10% H₂ and 5% CO](image)

**Figure 26: Experimental outputs in 10% H₂ and 5% CO**

- **Tested in 10% hydrogen and 15% carbon monoxide**

  When the target gas was 10% hydrogen and 15% carbon monoxide mixture, the output voltage of TCS kept going down rapidly until the 20th second (started from the 9th second); it reached a voltage of -55 mV and then kept relatively stable, as shown in Figure 27.
The experimental result and analysis of experiment 2

The experimental result of this experiment is in Table 21. The sampling time was 10 seconds after the stable point. To make it more convenient, the “measured value” in this table is the absolute value of the output reading. The results of experiment 2 are plotted in Figure 28.

Table 21: Results of experiment 2 at 24°C±3°C

<table>
<thead>
<tr>
<th>Experiment2</th>
<th>10% H₂</th>
<th>10% H₂ 2% CO</th>
<th>10% H₂ 5% CO</th>
<th>10% H₂ 15% CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>56.12 mV</td>
<td>58.28 mV</td>
<td>60.59 mV</td>
<td>55.78 mV</td>
</tr>
</tbody>
</table>

From Figure 23 and Figure 11, it can be seen that the trends of these two curves are very similar. The unit-removed values of experimental results were calculated by using equation 11 and 12 and listed in Table 22. The calculated values and experimental
values were put into one plot in Figure 29. When comparing the experimental result with the calculated result, the trend is very similar and the values are also very close. It is the same as the simulation result that the gas mixture thermal conductivity is not sensitive to the carbon monoxide concentration change. The change can be ignored as it was introduced in the simplification method. Moreover, as it was tested in previous experiment, once the sensor output became stable, it stayed stable as long as the concentration remained the same.

![Graph showing the relationship between CO concentration and output voltage.]

**Figure 28: Results of experiment 2**

**Table 22: Calculated results of the unit-removed values of experiment 2**

<table>
<thead>
<tr>
<th>Experiment 2</th>
<th>10% H₂</th>
<th>10% H₂</th>
<th>10% H₂</th>
<th>10% H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated value W/(m·K)</td>
<td>0.0355</td>
<td>0.0351</td>
<td>0.0347</td>
<td>0.0345</td>
</tr>
<tr>
<td>Measured value</td>
<td>56.12 mV</td>
<td>58.28 mV</td>
<td>60.59 mV</td>
<td>55.78 mV</td>
</tr>
<tr>
<td>( V_{ur_mea} )</td>
<td>0.97</td>
<td>1.01</td>
<td>1.05</td>
<td>0.97</td>
</tr>
<tr>
<td>( V_{ur_cal} )</td>
<td>1.02</td>
<td>1.00</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>
5.3 Results and Analysis of Experiment - Tested in [H$_2$ + N$_2$] Gas Flows

In order to see that the TCS can distinguish different concentrations of H$_2$ in various gas flows, different concentrations of H$_2$ (diluted in nitrogen) gas mixtures have been tested in different flow rates. Experimental setup 2 and operational procedure 2 were used in the experiment:

a) 5%, 10%, 30% and 99.99% of H$_2$ (balanced in N$_2$) were tested;

b) Different flow rates: 2 LPM, 4 LPM, 6 LPM and 7 LPM

Reynolds number (Re) was used to evaluate whether there was turbulence during the detection. 100% of H$_2$ and 0% of H$_2$ (that would be 100% N$_2$) at 7 LPM flow rate were used to calculate the Reynolds numbers instead of 99.99% and 5% of H$_2$ (balanced in N$_2$). If there was no turbulence in pure H$_2$ and pure N$_2$ flows at 7 LPM, there would be...
no turbulence in 99.99% ~5% of H2 in gas flows at 0~7 LPM. Equation 13 was used to calculate Reynolds number.

The Re of H2 at 7 LPM was 58 and the Re of N2 at 7 LPM was 371. The fluid is laminar when its Re is less than 2300 [58]. The highest Re in the experiment was 371, which was much less than 2300, so there was no turbulence in the gas flows. Because the mean velocity of the gas flow was less than 0.1% of the speed of sound making the gas treated as incompressible [59], and the temperature and pressure were kept relatively constant, the gas flow was assumed to be in a relatively steady state and would not influence the experimental results.

\[
Re = \frac{\rho v D_H}{\mu}
\]

(13)

where,

\( Re \) = Reynolds number

\( \rho \) = the density of the fluid, kg/m³

\( v \) = the mean velocity of the fluid, m/s

\( D_H \) = the hydraulic diameter of the pipe, m

\( \mu \) = the dynamic viscosity of the fluid, Pa.s

<table>
<thead>
<tr>
<th>Density of N2 at 24°C</th>
<th>Density of H2 at 24°C</th>
<th>Viscosity of N2 at 24°C</th>
<th>Viscosity of H2 at 24°C</th>
<th>Hydraulic diameter</th>
<th>Mean velocity of the gas flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15 kg/m³</td>
<td>0.08 kg/m³</td>
<td>0.000018 Pa.s</td>
<td>0.000008 Pa.s</td>
<td>0.02 m</td>
<td>0.29 m/s</td>
</tr>
</tbody>
</table>

### 5.3.1 Tested in 5% Hydrogen Gas Flow

When the target gas was 5% hydrogen balanced in nitrogen and the flow rate was 2 LPM, the output voltage of TCS kept going down rapidly until the 79th second (started
from the 14th second. It reached a voltage of -28.27 mV and then kept relatively stable. The flow rate was increased to 4 LPM at the 171st second at which the output voltage was -29.02 mV, the voltage dropped down very slow. At the 291st second, the output voltage reached -29.61 mV and kept relatively stable.

The flow rate was increased again by 2 LPM which was set to 6 LPM at the 329th second at which the output voltage was -29.69 mV. The output voltage had few changes. At the 423rd second, when the output voltage was -29.77 mV, the flow rate was increased to 7 LPM. At the 498th second, the output voltage was -29.75 mV which was very close to the output voltage sampled at the 423rd second. The whole process is shown in Figure 30.

![Figure 30: 5% H₂ gas flow with flow rates from 0 ~7 LPM at 24°C±3°C](image-url)
5.3.2 Tested 10% Hydrogen Gas Flow

When the target gas was 10% hydrogen balanced in nitrogen and the flow rate was 2 LPM, the output voltage of TCS kept going down rapidly until the 87th second (started from the 19th second). It reached a voltage of -56.7 mV and then kept relatively stable. The flow rate was increased to 4 LPM at the 173rd second at which, the output voltage was -58.03 mV. The voltage dropped down very slow until the 233rd second, and then the output voltage reached -58.31 mV and kept relatively stable.

The flow rate was increased again by 2 LPM which was set to 6 LPM at the 304th second at which the output voltage was -58.51 mV. The output voltage had few changes and then at the 367th second, when the output voltage was -58.61 mV, the flow rate was increased to 7 LPM. At the 465th second, the output voltage was -58.75 mV which was very close to the output voltage sampled at the 367th second. The whole process is shown in Figure 31.

![Figure 31: 10% H₂ gas flow with flow rates from 0 ~ 7 LPM at 24°C±3°C](image-url)
### 5.3.3 Tested in 30% Hydrogen Gas Flow

When the target gas was 30% hydrogen balanced in nitrogen and the flow rate was 2 LPM, the output voltage of TCS kept going down rapidly until the 180th second (started from the 94th second). It reached a voltage of -152.69 mV and then kept relatively stable; the flow rate was increased to 4 LPM at the 291st second at which, the output voltage was -156.11 mV. The voltage dropped down very slow until the 374th second. The output voltage reached -157.81 mV and kept relatively stable.

The flow rate was increased again by 2 LPM which was set to 6 LPM at the 439th second at which the output voltage was -157.9 mV. The output voltage had few changes and then at the 521st second, when the output voltage was -157.98 mV, the flow rate was increased to 7 LPM. At the 582nd second, the output voltage was -158.03 mV which was very close to the output voltage sampled at the 521st second. The whole process is shown in Figure 32.

![Figure 32: 30% H₂ gas flow with flow rates from 0 ~7 LPM at 24°C±3°C](image)
5.3.4 Tested in 99.99% Hydrogen Gas Flow

When the target gas was 99.99% hydrogen balanced in nitrogen and the flow rate was 2 LPM, the output voltage of TCS kept going down rapidly until the 62\textsuperscript{nd} second (started from the 35\textsuperscript{th} second). It reached a voltage of -364.22 mV and then kept relatively stable. The flow rate was increased to 4LPM at the 215\textsuperscript{th} second at which, the output voltage was -371.87 mV. The voltage dropped down very slow until the 404\textsuperscript{th} second. The output voltage reached -373.30 mV and kept relatively stable.

The flow rate was increased again by 2 LPM which was set to 6 LPM at the 439\textsuperscript{th} second at which the output voltage was -373.46 mV. The output voltage had few changes and then at the 544\textsuperscript{th} second, when the output voltage was -373.71 mV, the flow rate was increased to 7 LPM. At the 685\textsuperscript{th} second, the output voltage was -372.81 mV which was very close to the output voltage sampled at the 544\textsuperscript{th} second. The whole process is shown in Figure 33.

![Graph showing output voltage over time with details of temperature and humidity](image)

Figure 33: 99.99\% H\textsubscript{2} gas flow with flow rates from 0 ~ 7 LPM at 24°C±3°C
5.3.5 The Experimental Result and Analysis of Experiment 3

The results of Experiment 3 are in Table 23. The output change was very little when the flow rate changed within 0 LPM ~ 7 LPM as it can be seen in Figure 34. The higher the concentration was, the less the change was as seen in Figure 35. When the concentration increased, the output decreased slightly when the flow rate was 7 LPM. When comparing the results between 0 LPM and other flow rates (2 LPM, 4 LPM, 6 LPM and 7 LPM), the difference was not very significant. For 5% of H₂, the output voltage increased 3.3%. For 10%, 30% and 99.99% of H₂, the output increased 2.2%, 1.8% and 0.5% respectively. Moreover, when the flow rate remained the same, the sensor output could also stay relatively stable. This is the same feature as seen in previous experiments.

<table>
<thead>
<tr>
<th>Flow rate (LPM)</th>
<th>5% H₂ (mV)</th>
<th>10% H₂ (mV)</th>
<th>30% H₂ (mV)</th>
<th>99.99% H₂ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>28.85</td>
<td>57.48</td>
<td>155.29</td>
<td>371.86</td>
</tr>
<tr>
<td>2</td>
<td>29.05</td>
<td>58.18</td>
<td>157.78</td>
<td>372.98</td>
</tr>
<tr>
<td>4</td>
<td>29.45</td>
<td>58.43</td>
<td>157.92</td>
<td>373.3</td>
</tr>
<tr>
<td>6</td>
<td>29.68</td>
<td>58.62</td>
<td>158.01</td>
<td>373.58</td>
</tr>
<tr>
<td>7</td>
<td>29.8</td>
<td>58.76</td>
<td>158.08</td>
<td>373.72</td>
</tr>
</tbody>
</table>

Table 24: Results of experiment 3 at 24°C±3°C
Figure 34: Flow rate vs. output voltages of different concentrations of H\textsubscript{2}

Figure 35: Output voltage change rate in 7 LPM gas flow
5.4 Experiment 4 - Tested at Constant Temperatures and Constant RH

In this experiment, how much influence the temperature change can bring about was tested. How much influence the relative humidity change can bring to the sensor was also tested. Experimental setup 3 was used in experiment 4.

- **Constant Temperatures**

Three different temperatures were tested:

- At 31°C, RH from 37% ~ 61% a
- At 26.5°C, RH from 68% ~ 78% ~ 73%
- At 24.4°C, RH from 72% ~ 56%

The results are showed in Table 24, Table 25 and Table 26 respectively and are plotted in Figure 36, Figure 37 and Figure 38.

| Output (mV) | 3.97 | 4.13 | 4.27 | 4.39 | 4.52 | 4.68 | 4.79 | 4.87 | 4.97 |
| RH | 37% | 39% | 41% | 42% | 44% | 46% | 48% | 50% | 52% |
| Output (mV) | 5.02 | 5.1 | 5.16 | 5.18 | 5.26 | 5.28 | 5.35 | 5.41 | 5.39 |
| RH | 53% | 54% | 55% | 56% | 57% | 58% | 59% | 60% | 60% |
| Output (mV) | 5.38 | 5.41 | 5.46 | 5.41 | 5.43 | 5.45 | 5.42 | 5.43 | 5.41 |
| RH | 60% | 60% | 61% | 61% | 61% | 61% | 61% | 61% | 61% |
| Output (mV) | 5.40 | 5.39 | 5.41 | 5.40 | 5.39 | 5.39 | 5.37 | 5.37 | 5.39 |
| RH | 61% | 61% | 61% | 61% | 61% | 61% | 61% | 61% | 61% |
Figure 36: Outputs vs. RH at 31 °C

Table 26: Results at 26.5±1.5 °C while RH varied from 68% ~78% ~73%

<table>
<thead>
<tr>
<th>Output (mV)</th>
<th>4.95</th>
<th>5.05</th>
<th>5.13</th>
<th>5.19</th>
<th>5.28</th>
<th>5.44</th>
<th>5.51</th>
<th>5.59</th>
<th>5.67</th>
<th>5.71</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>68%</td>
<td>70%</td>
<td>71%</td>
<td>73%</td>
<td>74%</td>
<td>75%</td>
<td>76%</td>
<td>76%</td>
<td>77%</td>
<td>77%</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>5.87</td>
<td>5.88</td>
<td>5.95</td>
<td>5.89</td>
<td>5.96</td>
<td>5.89</td>
<td>5.96</td>
<td>5.96</td>
<td>5.92</td>
<td>5.95</td>
</tr>
<tr>
<td>RH</td>
<td>77%</td>
<td>77%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>5.90</td>
<td>5.92</td>
<td>5.94</td>
<td>5.93</td>
<td>5.91</td>
<td>5.88</td>
<td>5.85</td>
<td>5.82</td>
<td>5.70</td>
<td>5.60</td>
</tr>
<tr>
<td>RH</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>78%</td>
<td>77%</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>5.64</td>
<td>5.59</td>
<td>5.53</td>
<td>5.46</td>
<td>5.40</td>
<td>5.38</td>
<td>5.41</td>
<td>5.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RH</td>
<td>77%</td>
<td>76%</td>
<td>75%</td>
<td>75%</td>
<td>74%</td>
<td>74%</td>
<td>74%</td>
<td>73%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 37: Outputs vs. RH at 26.5 °C

Table 27: Results at 24.4±0.5 °C while RH varied from 72% ~ 56%

<table>
<thead>
<tr>
<th>Output (mV)</th>
<th>5.21</th>
<th>5.17</th>
<th>5.18</th>
<th>5.13</th>
<th>5.17</th>
<th>5.10</th>
<th>4.96</th>
<th>4.88</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH</td>
<td>72%</td>
<td>72%</td>
<td>72%</td>
<td>72%</td>
<td>72%</td>
<td>72%</td>
<td>70%</td>
<td>69%</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>4.76</td>
<td>4.70</td>
<td>4.60</td>
<td>4.48</td>
<td>4.43</td>
<td>4.32</td>
<td>4.27</td>
<td>4.25</td>
</tr>
<tr>
<td>RH</td>
<td>68%</td>
<td>67%</td>
<td>66%</td>
<td>65%</td>
<td>64%</td>
<td>64%</td>
<td>63%</td>
<td>62%</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>4.24</td>
<td>4.18</td>
<td>4.20</td>
<td>4.16</td>
<td>4.11</td>
<td>4.08</td>
<td>4.10</td>
<td>4.10</td>
</tr>
<tr>
<td>RH</td>
<td>62%</td>
<td>62%</td>
<td>61%</td>
<td>60%</td>
<td>59%</td>
<td>58%</td>
<td>57%</td>
<td>56%</td>
</tr>
</tbody>
</table>
Figure 38: Outputs vs. RH at 24.4 °C

- **Constant RH**

RH was set to 62% and temperature swept. The results are showed in Table 27 and plotted in Figure 39.

Table 28: Results at 62% ± 1% RH while temperature varied from 33.2 °C ~ 27.0°C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Temperature (°C)</th>
<th>Output (mV)</th>
<th>Temperature (°C)</th>
<th>Output (mV)</th>
<th>Temperature (°C)</th>
<th>Output (mV)</th>
<th>Temperature (°C)</th>
<th>Output (mV)</th>
<th>Temperature (°C)</th>
<th>Output (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.2</td>
<td>33.1</td>
<td>5.39</td>
<td>33.0</td>
<td>5.37</td>
<td>32.7</td>
<td>5.37</td>
<td>32.4</td>
<td>5.39</td>
<td>32.0</td>
<td>5.33</td>
</tr>
<tr>
<td>31.7</td>
<td>31.44</td>
<td>5.30</td>
<td>31.7</td>
<td>5.32</td>
<td>31.44</td>
<td>5.32</td>
<td>31.44</td>
<td>5.32</td>
<td>31.44</td>
<td>5.32</td>
</tr>
<tr>
<td>30.4</td>
<td>30.3</td>
<td>5.22</td>
<td>30.7</td>
<td>5.20</td>
<td>30.3</td>
<td>5.20</td>
<td>30.3</td>
<td>5.20</td>
<td>30.3</td>
<td>5.20</td>
</tr>
<tr>
<td>29.7</td>
<td>29.6</td>
<td>5.15</td>
<td>29.7</td>
<td>5.19</td>
<td>29.6</td>
<td>5.19</td>
<td>29.6</td>
<td>5.19</td>
<td>29.6</td>
<td>5.19</td>
</tr>
<tr>
<td>29.5</td>
<td>29.4</td>
<td>5.16</td>
<td>29.5</td>
<td>5.16</td>
<td>29.4</td>
<td>5.16</td>
<td>29.4</td>
<td>5.16</td>
<td>29.4</td>
<td>5.16</td>
</tr>
<tr>
<td>29.1</td>
<td>29.0</td>
<td>5.16</td>
<td>29.2</td>
<td>5.14</td>
<td>29.0</td>
<td>5.14</td>
<td>29.0</td>
<td>5.14</td>
<td>29.0</td>
<td>5.14</td>
</tr>
<tr>
<td>28.1</td>
<td>28.1</td>
<td>5.08</td>
<td>28.1</td>
<td>5.06</td>
<td>28.0</td>
<td>5.06</td>
<td>28.0</td>
<td>5.06</td>
<td>28.0</td>
<td>5.06</td>
</tr>
<tr>
<td>27.7</td>
<td>27.6</td>
<td>5.04</td>
<td>27.7</td>
<td>5.00</td>
<td>27.6</td>
<td>5.00</td>
<td>27.6</td>
<td>5.00</td>
<td>27.6</td>
<td>5.00</td>
</tr>
<tr>
<td>27.3</td>
<td>27.2</td>
<td>4.98</td>
<td>27.3</td>
<td>4.98</td>
<td>27.2</td>
<td>4.98</td>
<td>27.2</td>
<td>4.98</td>
<td>27.2</td>
<td>4.98</td>
</tr>
<tr>
<td>27.0</td>
<td>27.0</td>
<td>4.98</td>
<td>27.0</td>
<td>4.98</td>
<td>27.0</td>
<td>4.98</td>
<td>27.0</td>
<td>4.98</td>
<td>27.0</td>
<td>4.98</td>
</tr>
</tbody>
</table>
The Experimental Result and Analysis of Experiment 4

When the temperature was 31 °C and the RH increased from 37% to 61%, the output voltage increased as the RH rose as shown in Table 24 and Figure 36. When the temperature was 26.5 °C, the RH increased from 68% to 78% and then went down to 73%. The output voltage increased as the RH increased. When the RH went down, the output voltage also went down accordingly as shown in Table 25 and Figure 37. When the temperature was 24.4 °C, the RH decreased from 72% to 56%, the output voltage decreased as the RH decreased as shown in Table 26 and Figure 38. When the RH was 62%, the temperature decreased from 33.2 °C ~ 27 °C, and the output voltage also went down as shown in Table 27 and Figure 39.
5.5 Experiment 5-Zero Drift

The signal level may vary from its set zero value when the sensor is working. This introduces an error into the measurement equal to the amount of drift which is called zero drift. In this experiment, how many zero drifts the sensor has in current condition has been tested. Different sensors may have different zero drift, but this result can be a reference. Experimental setup 3 was used. In current research, it is not investigated that whether the zero drift is sensitive to factors as temperature, pressure and relative humidity.

➢ Tested zero drift

The reference gas in the tested sensor was standard air. The RH was 62% and the temperature at the beginning was 29°C at the time the experiment started. The output was read 0.9 mV, so 0.9 mV was assumed to be the zero of the sensor output in the experiment (the output can be set to zero by adjust the varistor in the bridge circuit). The sensor operated in this condition for three hours.

➢ The experimental result and analysis of experiment 5

After 3 hours running, the temperature went up by 1.4°C to 30.4°C and the output also went up by 1.57 mV to 2.47 mV, as shown in Table 28 and Figure 40. When the hydrogen concentration was no more than 30%, the “voltages per 1% hydrogen” values which were calculated by (measured value) / (hydrogen concentration in vol.) were very close as shown in Table 29. Therefore, assume that the thermal conductivity is a linear change when hydrogen concentration increases in experiment 1. When the concentration is no greater than 30%, for every 1% of hydrogen concentration increasing, the output voltage of the sensor increases about 5.1mV. Thus, the 1.57 mV drift will bring 0.31% (1.57/5.1*1%=0.31%) of hydrogen concentration error in volume.
Table 29: Zero drifts while temperature varied

<table>
<thead>
<tr>
<th>Output (mV)</th>
<th>0.9</th>
<th>0.9</th>
<th>0.89</th>
<th>0.92</th>
<th>0.95</th>
<th>0.99</th>
<th>1.02</th>
<th>1.00</th>
<th>1.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>29</td>
<td>29</td>
<td>29.1</td>
<td>29.1</td>
<td>29.1</td>
<td>29.2</td>
<td>29.3</td>
<td>29.3</td>
<td>29.4</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>1.15</td>
<td>1.17</td>
<td>1.22</td>
<td>1.27</td>
<td>1.31</td>
<td>1.43</td>
<td>1.53</td>
<td>1.64</td>
<td>1.73</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>29.6</td>
<td>29.6</td>
<td>29.6</td>
<td>29.7</td>
<td>29.7</td>
<td>29.9</td>
<td>29.8</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>1.74</td>
<td>1.73</td>
<td>1.83</td>
<td>1.91</td>
<td>2.01</td>
<td>2.05</td>
<td>2.08</td>
<td>2.11</td>
<td>2.13</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>30.0</td>
<td>30.1</td>
<td>30.1</td>
<td>30.2</td>
<td>30.2</td>
<td>30.3</td>
<td>30.3</td>
<td>30.4</td>
<td>30.4</td>
</tr>
<tr>
<td>Output (mV)</td>
<td>2.19</td>
<td>2.24</td>
<td>2.24</td>
<td>2.35</td>
<td>2.34</td>
<td>2.39</td>
<td>2.43</td>
<td>2.44</td>
<td>2.47</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>30.2</td>
<td>30.3</td>
<td>30.2</td>
<td>30.4</td>
<td>30.4</td>
<td>30.4</td>
<td>30.4</td>
<td>30.4</td>
<td>30.4</td>
</tr>
</tbody>
</table>

Table 30: Voltages per 1% hydrogen

<table>
<thead>
<tr>
<th>Measured value</th>
<th>5% H₂</th>
<th>10% H₂</th>
<th>30% H₂</th>
<th>99.99% H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltages per 1% hydrogen</td>
<td>5.064 mV</td>
<td>5.612 mV</td>
<td>5.128 mV</td>
<td>3.65 mV</td>
</tr>
</tbody>
</table>

Figure 40: Zero drifts at R.H. = 28.6% ± 0.2%
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

6.1 Summary of Contributions

In this thesis, the currently commercialized hydrogen sensors have been reviewed. How these sensors are used in current automotive applications has been discussed. Hydrogen used as an additional fuel to reduce vehicle emissions has also been discussed but no dedicated sensors have been produced for this application from manufacturers. The properties of hydrogen and hydrogen sensors have been investigated in order to decide which one, if any, is suitable to be used in this specific application.

Comparisons were made and the thermal conductivity sensor was selected and studied because of its: board range of measurement, resistance of carbon monoxide and immunity of hydrogen sulfide. The measurability of hydrogen by using its thermal conductivity property was verified by simulation and experiments. Different thermal conductivity was obtained in the simulation and different sensor voltage outputs were obtained in the experiment when the hydrogen concentration (balanced in nitrogen) was changed. The sensor output voltage was very close to linear when the hydrogen concentration was below 30% in volume. The output was around 5.2 mV per 1% hydrogen balanced in nitrogen (only for the sensor tested in this research).

The carbon monoxide, as the main interference gas for hydrogen detection in automotive application, was also simulated and tested in experiment. No significant influence was seen in the simulation and experiment. In the simulation, when 15% carbon monoxide was mixed with 30% hydrogen balanced in nitrogen, the gas mixture thermal
conductivity was 0.0566 W/(m·K) while 30% hydrogen balanced in nitrogen without carbon monoxide was 0.0573 W/(m·K). The difference between them (compared to 30% hydrogen without carbon monoxide) was 1.2%. When 15% of carbon monoxide was mixed with 10% hydrogen balanced in nitrogen, the gas mixture thermal conductivity was 0.0345 W/(m·K) while 10% of hydrogen balanced in nitrogen without carbon monoxide was 0.0355 W/(m·K). The difference between them (compared to 10% hydrogen without carbon monoxide) was 2.8%. When hydrogen was set to 10%, carbon monoxide changed to 2%, 5%, 15% and 60%, the differences were 1.1%, 2.3%, 2.8% and 3.9% respectively. This demonstrated that the carbon monoxide could influence the detection of hydrogen but not much. For 10% hydrogen detection, 60% carbon monoxide gave 3.9% error. When hydrogen concentration increased, the influence of carbon monoxide decreased. When carbon monoxide concentration increased, the influence increased if the hydrogen concentration kept unchanged.

In the experiment, both the resistance of the sensor to carbon monoxide and the influence of the carbon monoxide on the sensor were demonstrated. When 10% hydrogen mixed with 2%, 5% and 15% of carbon monoxide (balanced in nitrogen), the outputs were 58.28 mV, 60.59 mV and 55.78 mV respectively while 10% hydrogen (balanced in nitrogen) without carbon monoxide was 56.12 mV. They were very close to what they were supposed to be. However, the absolute differences (compared to 10% hydrogen without carbon monoxide) were 3.8%, 7.9% and 0.6% respectively, which were much higher than the values in the simulation (1.1%, 2.3%, and 2.8%). If the maximum value 7.9% was converted to volume of hydrogen, it was 0.79% of hydrogen in volume.
When tested in gas flows, the sensor outputs were influenced by the gas flow rates during the experiments but not significantly. The Reynolds numbers of all the gas flow tested were below 371, so there was no turbulence. Because the mean velocity of the gas flow was less than 0.1% of the speed of sound, and the temperature and pressure were kept relatively constant, the gas flow was assumed to be in a relatively steady state and would not influence the experimental results. As the flow rate increased, the sensor output increased accordingly but they were increasing at different rates. The sensor output increased much slower. When 5% hydrogen (balanced in nitrogen) was tested at a flow rate up to 7 LPM, the relative voltage output increased 3.3% compared with 0 LPM. For 10% hydrogen tested in the same condition, the increase was 2.2%. When 30% hydrogen was tested, 1.8% increase was seen. When 99.99% hydrogen was tested, 0.5% increase was obtained. Thus, the influence of the gas flow rate decreased when the hydrogen concentration increased.

The stability of the sensor output signal was shown in experiment 1, 2 and 3. Once the output became relatively stable, it would stay stable as long as the condition remained the same. This feature is very important for signal sampling.

Water vapor influences most sensors and this was also seen when the thermal conductivity sensor was tested in the experiment. The sensor output changed along with the change in RH. At 26.5 °C, when the RH increased from 68% to 78%, the output voltage increased from 4.95 mV to 5.90 mV. When the RH kept relatively stable at 78%, the output voltage also remained relatively stable at around 5.90 mV. When the RH went down to 73%, the output voltage went down to 5.32 mV accordingly. At different temperatures, it was also the case. At 31 °C, when the RH increased from 37% to 61%,
the output voltage increased from 3.97 mV to 5.39 mV. At 24.4 °C as the RH decreased from 72% to 56%, the output voltage decreased from 5.21 mV to 4.10 mV. Thus, the influence of RH was obvious. Positive correlations between the output voltage and the RH existed.

The zero drift was also tested and the drift was seen. As the temperature increased, the zero point also increased. When the temperature was 29°C, the output was 0 mV. When the temperature went up to 30.4°C, the output became 1.57 mV. It seemed that the zero drift had been caused by the temperature change. More verification will be done in the future work because, other than the temperature and the relative humidity, factors like the pressure and electronics stabilizing were not monitored. They all may contribute to the zero drift.

6.2 Future Work

More component gases can be added to the target gas mixture to investigate the response of the thermal conductivity sensor and to verify the method of the simplification. Gas mixture with lower hydrogen concentrations such as less than 1% of hydrogen can be explored. Furthermore, flow rates higher than 7 LPM can be tested to see how sensitive the sensor is at these flow rates. The resistance of the sensor to hydrogen sulfide poisoning can also be test. When testing the impact of the temperature variation, wider temperature range above 30 °C can be explored. Zero drift may also be tested in different temperatures, different pressures and different relative humidity to find out the influence by each of them. The errors from estimations, equations, simplifications and zero drifts are all need to be calculated respectively. Moreover, the total system error also needs to be investigated.
Sampling is also an important issue and it is directly related to the sensor working efficiency. In this thesis, the signal was sampled when the sensor gave a relatively stable output. It can also be sampled at a constant time interval. More experiments can be done to compare these two methods. Same experiments can also be done in gas flows to see if the gas flow rates can also affect the sampling time.

Furthermore, if considering using the thermal conductivity sensor on a vehicle, how to filter out the unwanted substances such as water, soot and unburned hydrocarbons needs to be investigated. How to control the target gas temperature and flow rate needs to be found out. Electromagnetic compatibility including signal noise from the vehicle engine exhaust environment also needs to be studied.
REFERENCES


34. ”Datasheet of Metal oxide Semiconductor Gas Detector Elements”, e2v.


Weijun Deng was born in 1973 in Hubei Province, P.R. China. He received his MSc degree in electrical engineering from Oregon Science and Health University in Oregon, USA in 2001. He worked as an electronics engineer and a hardware engineer in automotive electronics industrial for several years. He joined the automotive sensor systems group in Dr. Jonathan Wu’s lab at University of Windsor in 2010.