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Miniature Gas Chromatography Development, Testing and Applications

Bidhya Kunwar

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MINIATURE GAS CHROMATOGRAPHY DEVELOPMENT, TESTING AND
APPLICATIONS

By

Bidhya Kunwar

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
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in the Department of Chemistry

Mississippi State, Mississippi

April 2011

MINIATURE GAS CHROMATOGRAPHY DEVELOPMENT, TESTING AND
APPLICATIONS

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Gas chromatography (GC) is a technique that includes all chromatographic processes in which a substance to be analyzed is in the gaseous state or is converted into such a state. Miniaturized GCs are in high demand due to their portability, ability to operate in the field, low power requirements and low material cost. The focus of this thesis is on the development, testing and applications of portable analytical instruments, specifically miniature gas chromatographs.

In the first chapter, two portable gas chromatograph prototypes are described; including a miniature GC and an auto sampling GC. The second chapter describes student experiment development that incorporates mini GCs into the academic chemistry curriculum and focuses on teaching principles of chromatography or use a gas chromatograph as a tool. The third chapter focuses on development, testing and application of a portable auto sampling prototype GC to aid in the production of biofuels.

DEDICATION

I would like to dedicate this to my parents Mr. Asha Kumar Kunwar and Mrs. Makhan Kunwar for their unconditional supports. I would not have reached this far without their support. I also dedicate this to my husband without whom I would have never worked towards achieving this degree and to my daughter for all her sacrifices.

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CHAPTER I

INTRODUCTION TO GAS CHROMATOGRAPHY

1.1 Introduction

Chromatography has gained enormous attention because of its simplicity and ability to separate complex mixtures of analytes to aid in their identification. Gas chromatography (GC) is a technique that includes all chromatographic processes in which a substance to be analyzed is in the gaseous state or is converted into such a state. Miniaturized GCs are in high demand due to their portability, ability to operate in the field, low power requirements and low material cost. The first part of the research described in this thesis is focused on the development of miniaturized portable gas chromatographs and the design of academic labs using a miniaturized GC. The second part of this thesis involves the biomass gasification process and online monitoring of the synthesis gas produced using an autosampling portable GC.

1.2 Background on Gas Chromatography

Gas chromatography was first introduced in 1952 by James and Martin. This analytical technique has become one of the most widely used and versatile analytical tools available in basic and applied research and in quality control.¹ The two basic types of gas chromatography are gas-liquid chromatography (GLC) and gas-solid chromatography (GSC). GC takes advantage of variable partition equilibrium therefore the separation is set by the affinity for the stationary phase and the solute vapor pressure. GSC uses adsorption equilibrium and is mostly used for gas analysis.²

1.3 Fundamentals of gas chromatography

Separation in GC occurs as the analytes interact with two phases: a stationary phase and a mobile phase. Stationary phases have different affinity for different analytes; therefore, elution time differs with different compounds. The mobile phase is utilized to push the analyte through the column.

The ability of stationary phase to retain a solute is given by

$$K = \frac{tr - tm}{tm} \quad \text{Equation 1.1}$$

Where tr is a retention time, tm is a dead time and K is retention factor.

The longer the solutes spend in the stationary phase the more likely it is to be separated from the components of similar volatility. The retention factor can be altered by changing the column or by temperature programming.

The selectivity factor (α) determines the ability of the column to separate the two components.

$$\alpha = \frac{tr(B) - tm}{tr(A) - tm} \quad \text{Equation 1.2}$$

Where $(tr)A$ and $(tr)B$ are the retention time of the components in a sample.

The resolution (R) of a column provides a quantitative measure of its ability to separate two components within a mixture.²⁻⁵

$$R = \frac{2(tr(B) - tr(A))}{WA + WB} \quad \text{Equation 1.3}$$

Where WA and WB are the width at the base of the associated peaks.

Factors like column length, internal diameter or particle size, and coating thickness of the stationary phase influence the separation and resolution of a column.

Peak spreading increases in proportion to the length of time the solute molecules stay on

the column. Therefore, a plate model is used to explain the efficiency of the column and similar to distillation, the higher the number of theoretical plates the higher the efficiency of the column. Separate equilibrations of the sample between the stationary and mobile phase occur in these "plates". The analyte moves down the column by transfer of equilibrated mobile phase from one plate to the next. The number of theoretical plate (N) is given by

$$N = 16 \left(\frac{t_r}{W} \right)^2 \quad \text{Equation 1.4}$$

The relation between the plate height (H) and length (L) of the column and number of theoretical plate (N) is given by:

$$H = \frac{L}{N} \quad \text{Equation 1.5}$$

1.4 Basic Design

The required components of gas chromatograph include: 1) Carrier gas; 2) Gas regulator and flow control; 3) Sample inlet; 4) Column; 5) Oven; 6) Detector; and 7) Data system.^{4, 5}

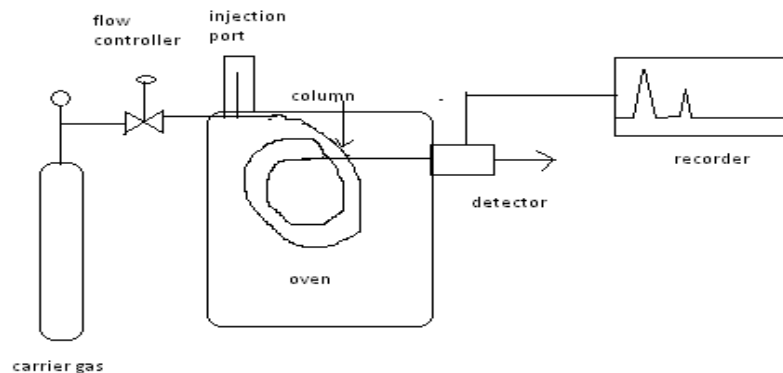


Figure 1.1 Gas Chromatograph

1.4.1 Carrier gas

The carrier gas is a mobile phase that is used to transport the sample in a column at a selected steady rate. Any gas that does not interfere with the properties of analyte and with the stationary phase is a suitable carrier gas. Generally, gases such as hydrogen, nitrogen, helium, and argon are used as a carrier gas. Other gases may also be used such as air and oxygen in certain cases. However, their use is limited by the possibility of reaction with the stationary phase and with the components of the sample.²

1.4.2 Pressure regulator and flow controller

The measurement and control of the carrier gas flow is essential for optimal column efficiency and for qualitative analysis. The plate model supposes that the chromatographic column contains a large number of separate layers which can be achieved by controlling carrier gas flow rate. Column efficiency depends on the proper linear gas velocity and can be easily determined by changing the flow until the maximum plate number is achieved. For qualitative analysis, it is essential to have a constant and reproducible flow rate so that retention times can be reproduced.⁴ Pressure regulators are used to maintain an adjustable constant pressure. Low range devices can be utilized to give finer regulation.⁵ With these devices the pressure is controlled by connecting a two-stage regulator to the carrier gas cylinder to reduce the tank pressure 2,500 psig down to a useable level of 20-60 psig.

1.4.3 Inlet system

In GC, it is critical that the sample is instantly vaporized and carried into the column. Poor (slow) vaporization can lead to peak tailing. There are four method of injections; split, splitless, direct, and cool on-column injections method. In split mode,

most of the sample will pass out the split vent to atmosphere and only a small proportion will flow into the column. This mode is suitable for concentrated samples. In splitless mode, most of the sample will be transferred onto the column rather than out the split vent. Splitless injection is suitable for trace level determinations i.e. in situations where the analytes may be in the concentration range of low ppm, $\mu\text{g/mL}$. In direct injection mode, the entire sample is injected into the heated injection liner. In cold on column mode, the sample can be discharged directly into the column or the column packing by means of a syringe.²

1.4.4 Column

The column is the heart of the chromatography. A column can be made up of stainless steel, copper, aluminum, or glass; however, fused silica is the most popular.⁴ Columns generally fall into two categories, capillary and those that are packed. Packed columns are generally 0.5 to 6 m length with inner diameters of 1 to 6 mm whereas capillary columns are usually 30 to 100 m with inner diameter of 0.1 to 1 mm.¹⁻³ Diatomaceous earth, ShinCarbon ST, etc. can be used as a packing material.²

A capillary column (also known as an open tubular (OT) column) is an empty tube whose inner wall is coated with adsorbent polymer.¹ Capillary columns have better efficiency than packed column.² Today, it is estimated that over 80% of all applications are run on capillary columns.⁴

1.4.5 Stationary phase

The inner wall of the capillary column is coated with a stationary phase. This stationary phase may be polar or non-polar.² Stationary phase such as squalane, apiezon grease, poly (ethylene glycol) phase (PEG), 100%poly (dimethyl siloxane), 5%poly

(diphenyl dimethyl siloxane), polyamide, polyimide are commonly used and commercially available.^{2,3} The thickness of these coatings are generally between 0.1-3.0 μm .

1.4.6 Detector

Many types of detectors are used in gas chromatography ranging from very selective to universal. Selective detection systems can be used to provide selective responses to particular groups of compounds to simplify the chromatograms from complex samples. The non-selective or universal detector responds to all compounds. Selective detectors respond to a range of compounds, which have some common chemical and physical property. The most common and popular detectors used in GC are flame ionization detector (FID) and thermal conductivity detector (TCD).⁵

Flame ionization detector (FID) is easy to use, gives very stable responses and is sensitive to most organic compounds. The column effluent is burned in a small oxygen-hydrogen flame producing ions in the process. A potential of a few hundred volts is applied across the burner tip and a collector electrode is located above the flame. The resulting current is measured.

The thermal conductivity detector (TCD) is a universal detector able to detect any compound that has a different thermal conductivity to the carrier gas.¹⁻⁵ It uses either a hot wire or thermistor as a sensing element. The resistance of the device changes relative to the reference stream of the pure carrier gas.

1.4.7 Temperature programming

Temperature programming is the process of controlling the column temperature during a GC run. It is very effective method for optimizing an analysis of a complex

mixture of chemicals. If a sample being analyzed by GC contains components whose boiling points extend over a wide range, it is more efficient to slowly increase the temperature during a run. Separation of analytes with a wide range of boiling points is significantly improved using temperature programming. By increasing the temperature the retention time is decreased. Increasing the temperature during the run decreases the partition coefficients of the analytes remaining on the column so that they move faster through the column, yielding decreased retention times.

1.5 Miniature Gas Chromatography

One major drawback with the conventional GC is that the required equipment is large, power intensive, and requires long analysis times.⁶ Miniaturization is one of the most noteworthy features of modern analytical instrumentation.⁷ GC is not an exception. The benefits of such miniaturized GC are obvious: they are portable and save material and power without sacrificing analytical performance. To date, several attempts at miniaturizing and micromachining GC instrumentation have been reported in literature.⁸⁻¹⁶ While most activities involve the fabrication and testing of capillary GC separation columns in silicon⁸⁻¹², of silicon-based injection systems and pre-concentrators¹³⁻¹⁷ or detectors.^{13, 18-23} One of the efforts towards GC miniaturization is the development of portable GC (transportable or handheld). Portable GC, as well as the miniaturization of GC instruments has been reviewed by Yashin et al.²⁴ In that review, a classification of portable GC was provided (Table 1.1). In most of the portable GCs developed so far, the bulky gas cylinder was discarded and filtered air is used as carrier gas.

Table 1.1 Classification of Portable Chromatographs (ref.²⁴)

Type	Purpose	Advantages, capabilities
Compact	For mobile and stationary laboratories	Saving of costs, power, materials, and space with analytical characteristics similar to those of stationary chromatographs, weight 10–25 kg
Portable, transportable, field	For on-site analysis	Small weight, rapid analysis, gas and power self-supporting, weight 5–15 kg
Chip-based chromatographs, silicon micromachining technology,, handheld, personal, pocket	For on-site analysis, handheld	For the fast resolution of relatively simple analytical problems, fully self-supporting, restricted analytical capabilities, weight 0.2–3 kg
Specially designed chromatographs, micro chromatographs	For space investigations	Automated analysis, small weight, resistant to impact and shaking

Portable GC devices using different detectors^{25, 26} have been developed, but their sensitivity and selectivity are limited, cost is high, and physical size is still bulky for many applications.⁶ As an effort to miniaturize GC, micromachined columns and preconcentrators have been investigated.²⁷ The fabrication of complete and working GC system prototypes based on Microelectromechanical systems (MEMS) components has only rarely been reported.^{18, 28} Cutting edge manufacture technologies have enabled producing silicon chip-based chromatographs and micromachined chromatographs.

Microelectromechanical systems (MEMS) technology based on the dielectric properties of pure silicon has matured. Using MEMS technology, one can fabricate miniature analytical devices.²⁹ Fabrication includes several steps: polishing of a silicon plate, oxidation to SiO₂, deposition of a photoresist, photolithography, etching of silicon oxide, the removal of the photoresist, and etching in the silicon microstructure.³⁰

1.6 Testing and Application Development of Novel Miniature Gas Chromatographs

1.6.1 Direct injection Mini GC with a single detector

Recent work aimed at reducing the size and weight of portable GC instruments and achieving autonomous operation of microfabricated vapor monitoring instruments has explored the use of vacuum-outlet GC with atmospheric pressure air as the carrier gas in order to eliminate the need for tanks of compressed gas.³¹⁻³⁵

Direct injection mini gas chromatographs and auto sampling gas chromatographs have been developed and evaluated as part of this thesis. The mini GC utilizes a MEMS chemicapacitive detection system for the detection of volatile organic compounds whereas the auto sampling GC is used for detection of combustible gases.

1.6.1.1 Chemicapacitor Detector and Detection theory

The chemicapacitor is an emerging sensing technology recently developed at Seacoast Science Company and used in prototype miniature gas chromatographs. A chemicapacitor can be configured as a conventional parallel-plate or interdigitated capacitor (Figure 1-2). In a chemicapacitor, the dielectric medium is an absorbent polymer. In operation, an electromagnetic field passes between the electrodes through the polymer. The interaction between the target analyte(s) and polymer modifies the dielectric properties of the polymer, resulting in a measurable capacitance change. When the polymer absorbs analyte the permittivity of the polymer changes, thereby altering the capacitance of the chemicapacitor.³⁶⁻³⁸

Chemicapacitance is best suited to detect highly polar compounds such as alcohols, ketones, and organic acids typical of organic solvents. Chemicapacitors are less well suited for detecting low-polarity compounds such as straight-chain hydrocarbons,

although by judicious choice of the absorbent polymer, one may detect low-polarity compounds such as hexane (typical compound in gasoline).³⁶

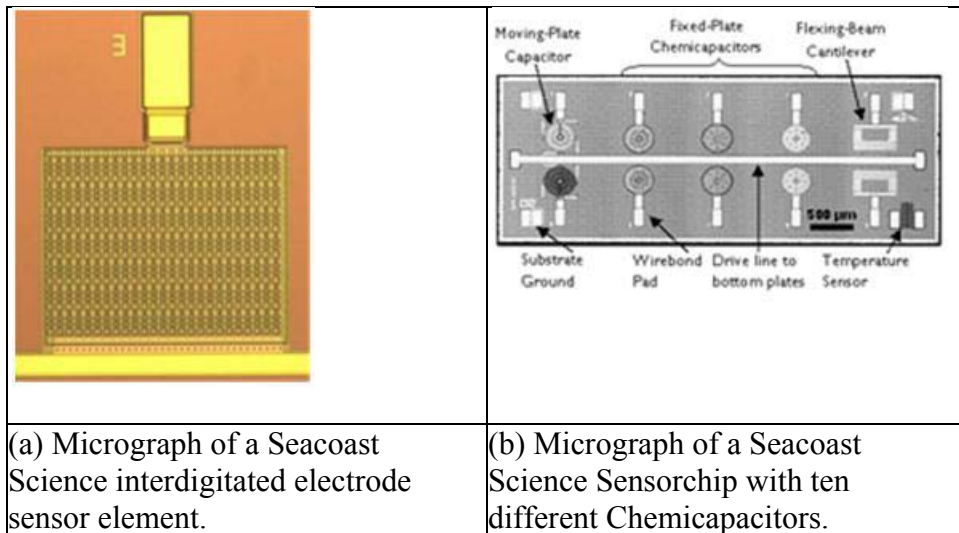


Figure 1.2 Sensor Element and Sensor Chips³⁶

An additional feature of the chemicapacitor detector is that the absorbent polymer may be tailored for a specific analyte or class of analytes. However, the signal from a chemicapacitor is a function of both the polarity of the analyte and the extent of absorption of analyte. The extent of analyte absorption depends on chemical properties of the polymer. For example, acidic polymers (Figure 1-3) tend to absorb basic analytes, whereas basic polymers tend to absorb acid analytes. Hansen solubility parameters^{39, 40} and Linear solvation energy relationships (LSER)^{40, 41} may be used to calculate relative strengths of bonding interactions, including the hydrogen bonding acid-base interactions.^{36, 38}

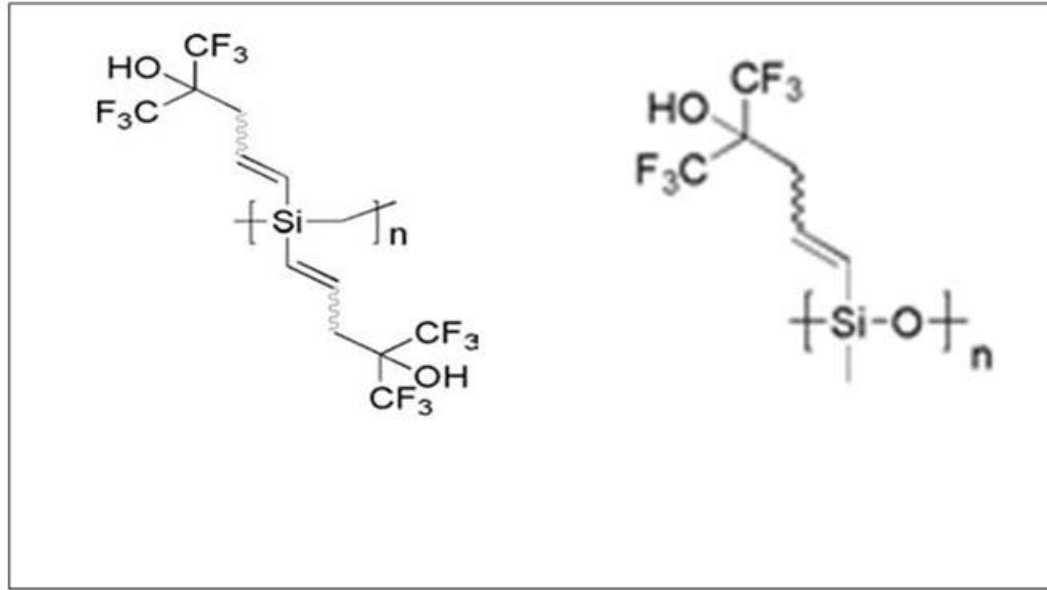


Figure 1.3 Acidic Siloxane Fluoroalcohol Polymers: Adiol (left) and SXFA (right)

Fluoroalcohols such as poly(siloxane fluoroalcohol) (SXFA) and poly(4-vinylhexafluorocumyl alcohol) (P4V) have very high acidity and, therefore, can interact strongly with analytes that are more basic. Poly(ethylene maleate) (PEM) and poly(ethylene imine) (PEI) are strongly basic polymers and will adsorb acidic analytes.³⁸

Seacoast's chemicapacitors are manufactured using modern micro-electromechanical system (MEMS) technology. This allows dramatically reduced size, weight, cost, and power requirements of analytical instruments. MEMS technology involves fabricating the detectors on a silicon chip. The MEMS chemicapacitors used in this study (Figure 1.4) are approximately 400 μ m long with parallel sense and drive electrodes. Electrodes in chemicapacitive sensors are coated with an analyte-specific polymer after final etching and cleaning of the sensor chip. The polymer is applied using micropipetting or ink jet technology. The polymer is water-insoluble, which improves the stability of the detector in operation.³⁶

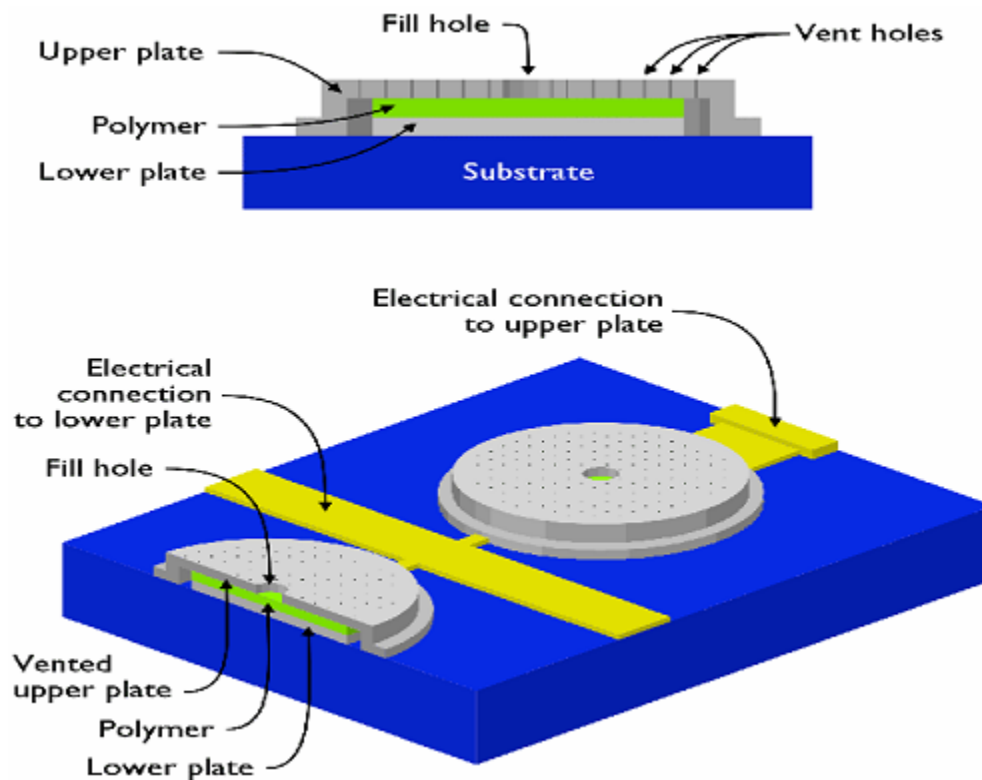


Figure 1.4 Parallel Plate MEMs Sensor

1.6.1.2 Chemicapacitor-Base Chromatograph

In the present work, we have combined and integrated two strategies, chemicapacitive sensor and chromatographic separation. The miniaturized GC developed with Seacoast includes the same components as most conventional gas chromatographs. However, recent advances at have allowed the development of a much smaller, portable system based on proprietary chemicapacitors as the detector. This concept uses a miniature pump to push ambient air through the chromatograph and thus frees the system from the need of a bottled compressed carrier gas. This significantly reduces system size compared to common GC detectors. However, the mini GC used in this study does have a port where a bottled carrier gas can be used if air sensitive samples are analyzed. Other commercially available portable GCs also use air as a carrier gas.^{33, 35}

The MEMS chemicapacitor used in this study employed a long lasting functionalized, hyper branched carbosilane polymer as the dielectric on the chemicapacitor. The MEMS chemicapacitor detector is compact and operates with very little power. The chemicapacitor also operates in ambient air without the need of compressed gases, thereby completely avoiding the bulky, hazardous gas cylinders typically required by gas chromatographs. The chromatographic column can be directly heated through resistance heating, eliminating the need for a large oven typical in gas chromatographs and reducing the space and power requirements. In the mini-GC (Figure 1.5), a sample is directly injected into the heated column which eliminates the need to heat the injection port. The column is an 11 m long metal capillary tube coated with a silicone medium i.e., polydimethylsiloxane (PDMS). The column in our GC acts in the same fashion as traditional GC columns: each component of a chemical mixture has a different affinity for the inner coating of the capillary column. Compounds with higher affinity for the coating travel more slowly through the column under the influence of the carrier gas. In a properly designed column, each compound exits the column separately. Column temperature and flow rate of the carrier gas can be adjusted to optimize separation of the components in a mixture. The capability of chromatography to separate components of a complex mixture is key to effective process control using chromatography.

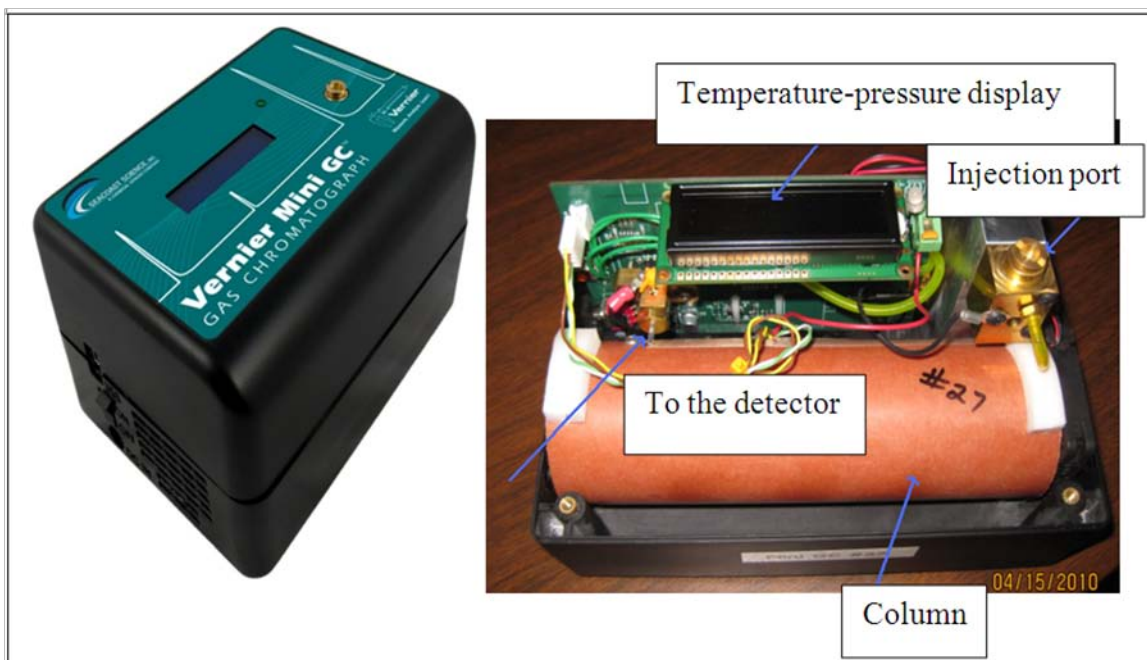


Figure 1.5 Mini GC with Chemicapacitor Detector

1.6.2 Auto Sampling Portable GC with multiple detectors

The second system (Figure 1.6) used in this thesis is being developed for real time chemical monitoring to track the production and composition of chemicals in real time. The auto sampling GC includes the same components as most conventional gas chromatographs with the addition of an automatic gas sampling loop. This prototype GC requires pressurized carrier gas input to push carrier gas (i.e. lab air) through the system. However, compressed air can be used as a carrier gas. Air gives the metal oxide sensor (MOS) more oxygen in order to improve the reproducibility of its response over time. Carrier gas is maintained at 40psi, which gave a flow rate of $\approx 10\text{mL}/\text{min}$. It has electrically actuated multi-position gas sampling valve and precise volume gas collection sample loop which can collect 2, 5 or 10 μL . Gas is separated by RestekShinCarbon ST 100/120 mesh packed (molecular sieve) 2 m long chromatographic column. A molecular sieve column separates analytes based on its molecular size. Two types of detectors are

present in this GC system; 1) MEMS chemicapacitor sensor array described above and 2) a metal oxide sensor (MOS). The system is modified to pull sample gas in with a pump and accept a pressurized carrier gas input. MOS respond to combustible gases like carbon monoxide, hydrogen and methane whereas the MEMS chemicapacitor sensor response to vapors of polar components such as ethanol but has low sensitivity to non-polar alkanes and aromatic compounds. Carbon dioxide and water did not produce responses on the MOS detector. The chemicapacitive sensor did not react to any of these gases. We presume that the lack of response to water shown by the chemicapacitive sensor is due to its absorption by the molecular sieve packing material in the micropacked permanent gas column, which has a high affinity for water. It includes the addition of EHC6WE software from Vici Valco Instrument Company controlled micro volume gas sampling valve that allows fine-tuning of sample gas flow and 10 μ L sample loop. It has ceramic filter for removal of tars and other particles from the sample gas. The whole thing is then assembled in a weatherproof polyethylene Pelican™ case as shown in the figure 1.7.

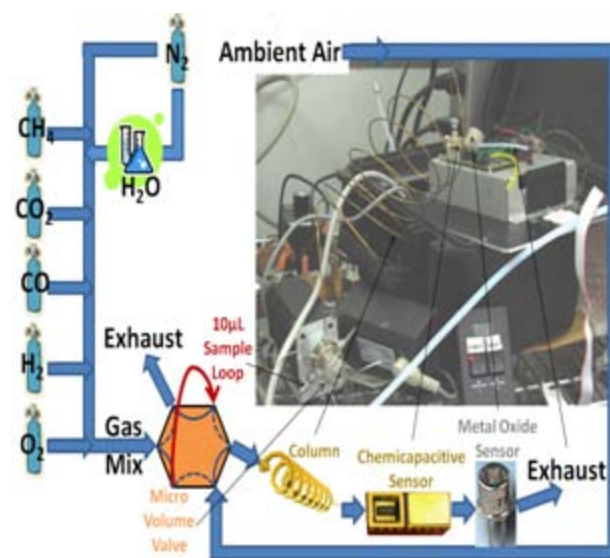


Figure 1.6 Components of Auto Sampling GC

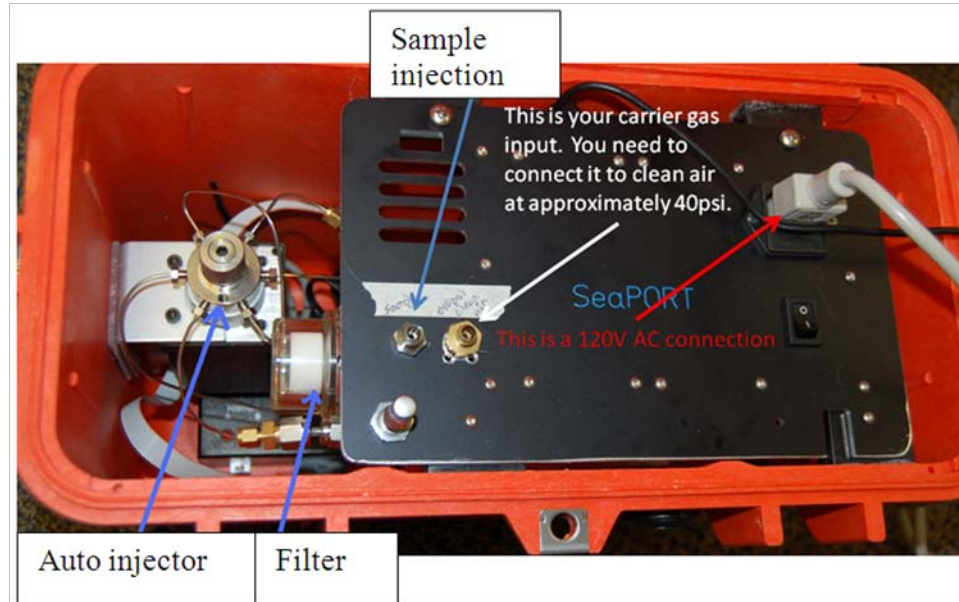


Figure 1.7 Seacoast Auto Sampling GC

1.6.2.1 Operating principle of metal oxide sensor

The MOS used in this study is a semiconductor gas sensor that has a sensing element containing sensing material and a heater used to heat the sensing element (e.g. 400 °C). Depending on target gas, the sensing element will utilize different materials such as tin dioxide (SnO_2), tungsten oxide (WO_3), etc. These sensors may be p-type or n-type. The presence of other gases with either reducing or oxidizing properties will further affect the density of charge carrier (n-types electrons or p-type holes) in the near-surface region. In the presence of an oxidizing gas, donor electrons in the crystal surface are transferred to the adsorbed oxidizing gas resulting in leaving positive charges in a space charge layer where as in the presence of a reducing gas, the surface density of the negatively charged increases. Therefore, the foreign gas molecules cause a decrease (reducing gases) or increase (oxidizing gases) of the depletion layer thickness by changing the surface-state density, which in turn leads to a change in the net conductance of the material.^{42, 43}

1.6.2.2 Operation of the auto sampling GC

A schematic of the two-position six-port low volume valve used in the GC can be seen in figure 1.8. The solid lines in the hexagon represent the normally open of the two valve positions, while the dash lines represent the “switched” valve position, used to deliver a sample to the column. Normally the sample is pulled onto the 10 μ l sample loop by the vacuum pump through a filter, and the clean air is pushed through the valve onto the column. When the valve is switched, whatever gas is in the sample loop is pushed on the column by the clean air stream and the vacuum pump pulls the gas mix through the filter directly to exhaust, bypassing the sample loop.

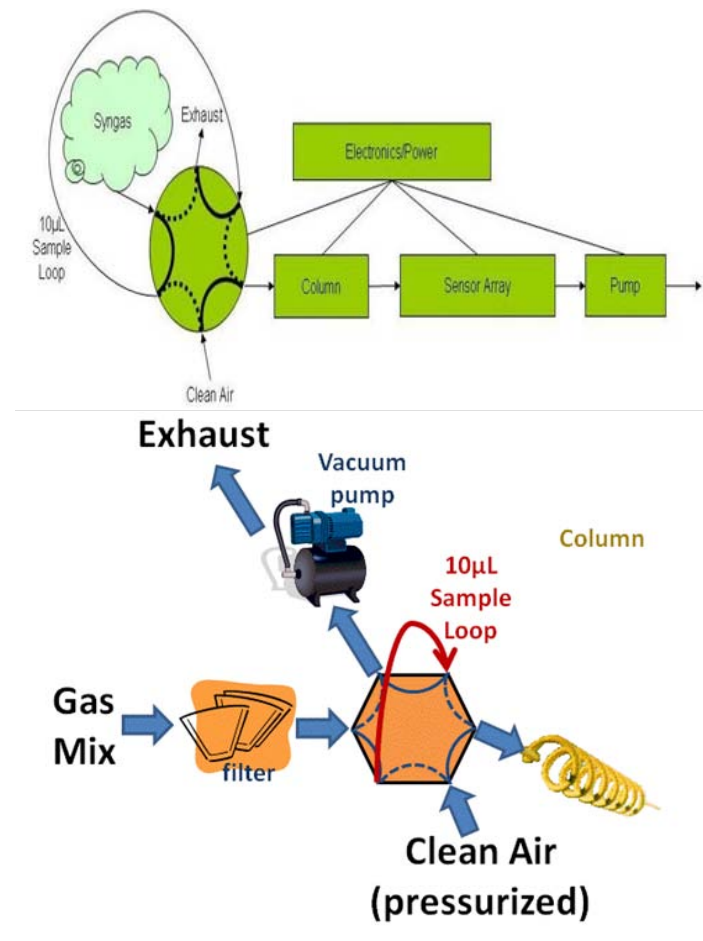


Figure 1.8 Operating Principle of Auto Sampling GC

1.7 Summary

This chapter has described the basics of the gas chromatography and the principles that govern its operation. It is important to understand this to be able to appreciate the work done in this project. Also described in this chapter are specific components of two prototype gas chromatographs used in this thesis. The work described in the subsequent chapters explains the approach towards developing a laboratory scale test gas chromatography.

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CHAPTER II
MINIATURE GAS CHROMATOGRAPHS IN ACADEMICS CHEMISTRY
LABORATORIES

2.1 Introduction

The focus of chapter 2 is to develop laboratory experiments that use the miniature gas chromatograph to teach undergraduates and high school students. Practical training on analytical equipment is very important for students as they prepare for chemically related careers or advanced study in related fields including biochemistry, materials science, forensic science, medicine, education, law, and other endeavors that may draw upon an understanding of the chemical basis of the world around us. Among techniques that are used for analytical purposes, gas chromatography is one of the most useful techniques. This technique is widely used for graduate research and in career-oriented fields for qualitative and quantitative analysis, therefore, it is very important for a student to understand the technique.

Seacoast Science supplied our laboratory with several prototype miniature gas chromatographs. These prototypes can be used by today's student to experience hands on learning with modern instrumentation. We began developing general chemistry laboratories for these units in order to teach various concepts. We have developed several experiments that incorporate this unit into the academic chemistry curriculum that focus on Principles of Chromatography or use a gas chromatograph as a tool for both semesters of General Chemistry and for Organic Chemistry. Several new labs have been developed

including those that teach the separation and quantification with chromatography, Raoult's Law and oxidation of an alcohol into a ketone. The range of detection capabilities of the Seacoast mini GC's is given in Table 2.1. The chromatograph can measure chemicals with the boiling point range of 20 °C to 200 °C. Temperature programming can be done to optimize separation of the analytes in the sample. Generally, for the experiments developed for this thesis, the temperature program start at a temperature between 30 °C to 40 °C (depending on the physical properties of analytes to be separated) and ramped to temperatures of 60 °C to 100 °C. This optimizes the separation of components from lower boiling points to higher boiling points. The mini GC's internal pump pressure in our experiments is set between 6-9 kPa. Low pressures decreases the flow rate of carrier gas which in turn increases elution times and thus enhance sample separation.

Table 2.1 Detection Capabilities of Mini GC

Compound family	Typical compounds	Range of acceptable boiling points
Alcohols	C ₁ -C ₈	65-195 °C
Aldehydes	C ₂ -C ₈	20-170 °C
Ketones	C ₃ -C ₈	55-175 °C
Carboxylic acids	C ₁ -C ₄	100-165 °C
Halogenated hydrocarbons	C ₁ -C ₈	65-160 °C
Esters	C ₂ -C ₁₀	30-120 °C
Ethers	C ₄ -C ₈	35-142 °C
Aromatic hydrocarbons	C ₆ -C ₁₂	80-165 °C
Nitriles	C ₂ -C ₅	80-140 °C

2.2 Experiments designed in our lab

2.2.1 Investigating Gas Chromatography

2.2.1.1 Objective

In our experiment, entitled 'Investigating Gas Chromatography' our goal was to develop a laboratory that teaches the basic principles of gas chromatography. The most important features of this experiment show how changing temperature and column pressure (flow) effects the chromatographic separations. In this experiment, one mixture containing nine compounds is tested repeatedly and the temperature and flow profile of the mini GC operation is varied to obtain the best possible separation of this mixture.

2.2.1.2 Procedure

The mixture of nine chemicals was prepared. The chemical present in the mixture is given in Table 2-2. The proportion of each of the analyte in the mixture was approximately the same. This mixture was injected in GC at different temperature-pressure values according to the set listed in the Table 2.3. The GC was run seven times with seven different conditions.

Table 2.2 Compounds used for Investigation of GC

Compound	Boiling point	Molecular weight
Methanol	64.7	32.05
Acetone	56.53	58.08
Methyl ethyl ketone	79.6	72.11
Ethyl acetate	77.1	88.10
2-hexanone	127.6	100.16
Propyl acetate	102.13	102
Butyl acetate	116.16	126
2-pentanone	86.13	101
4-methyl-2-pentanone	100.2	117

Table 2.3 Conditions used in GC for Different Runs

	Run1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Initial temperature	85 °C	85 °C	35 °C	35 °C	35 °C	35 °C	35 °C
Hold time (min)	10	10	10	3	3	2	3
Ramp rate °C/min	0	0	0	10	10	10	10
Final temperature	85 °C	85 °C	65 °C	65 °C	65 °C	75 °C	65 °C
Hold time (min)	0	0	0	7	1	5	4
Total length (min)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Pressure (kPa)	9.0	7.0	7.0	7.0	4.0	6.0	7.0

2.2.1.3 Result and Discussion

The seven chromatographs can be seen below. Figure 2.1 is the chromatogram obtained from a first run. The peaks are too close together and only four peaks appeared distinctly. The chromatogram has four peaks but two of the peaks have shoulders. The chromatogram from a second run is shown in figure 2.2. A second run was operated at lower pressure than first run and this reduced pressure helped to reveal more peaks. In second run 6-7 peaks are visible.

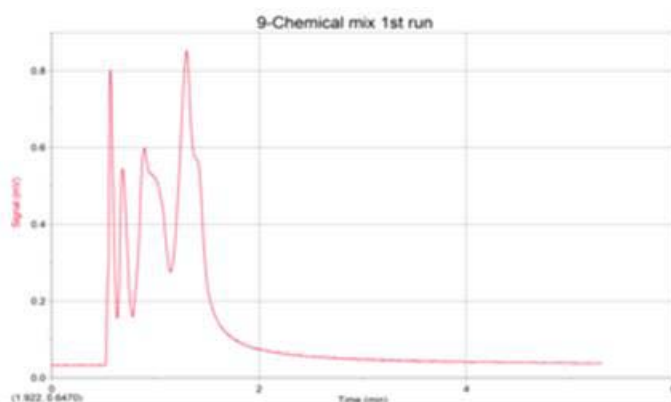


Figure 2.1 Chromatogram of First Run

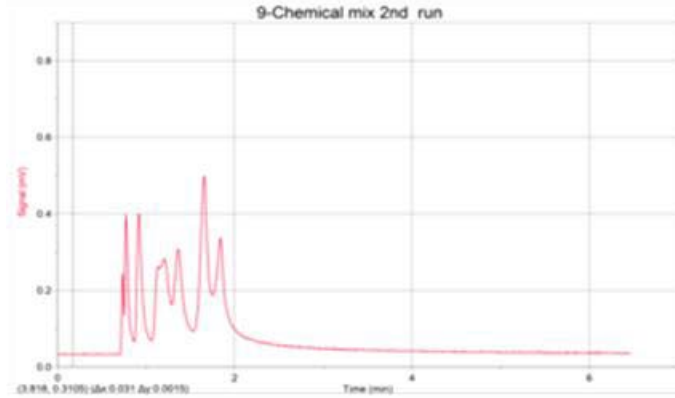


Figure 2.2 Chromatogram of Second Run

In run three, the temperature was reduced which made 8 peaks visible. In the fourth run temperature ramping was done. With temperature ramping, the peak for 9th chemical appeared. By decreasing the temperature of the column the sample may separate properly but takes longer time to elute. By using temperature programming, each component can be separated and is seen in the chromatogram because each component has different boiling points.

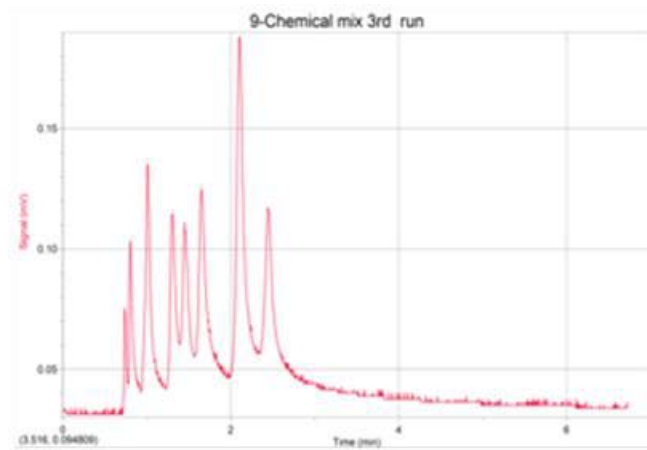


Figure 2.3 Chromatogram of Third Run

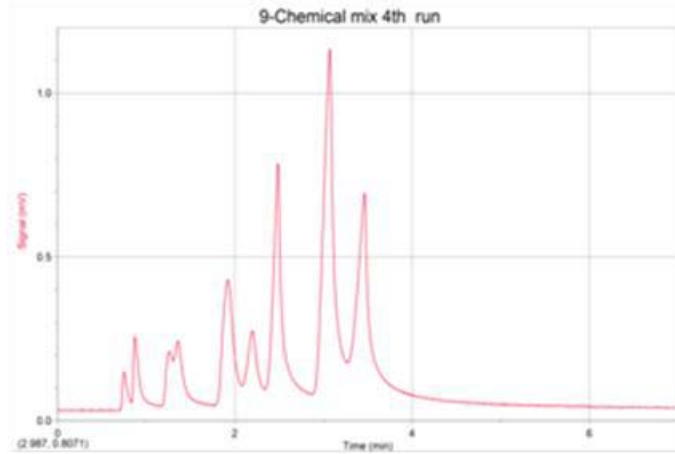


Figure 2.4 Chromatogram of Forth Run

In the fifth run, there is a good separation of the peaks, but the run stopped before all nine peaks appeared. For a fifth run the pressure was 4 kPa and the final hold was 1 min and at lower pressure, analytes elute slowly and therefore, there was not enough time for a complete run. The peaks from sixth run are best so far, because all nine peaks appeared in the chromatogram, but peak intensities are low.

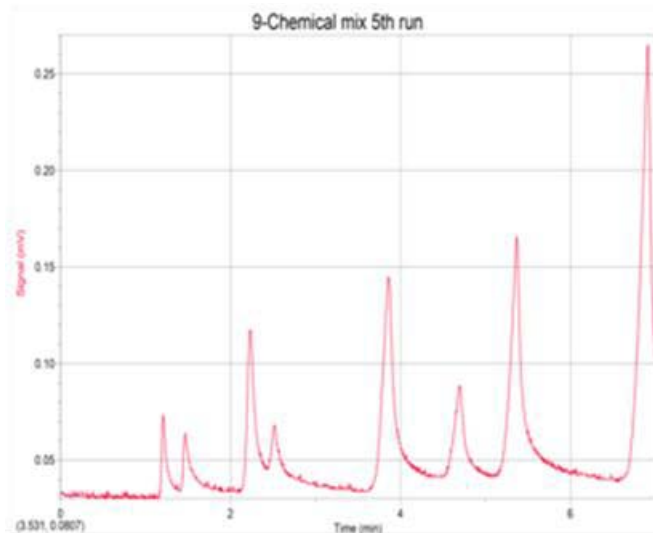


Figure 2.5 Chromatogram of Fifth Run

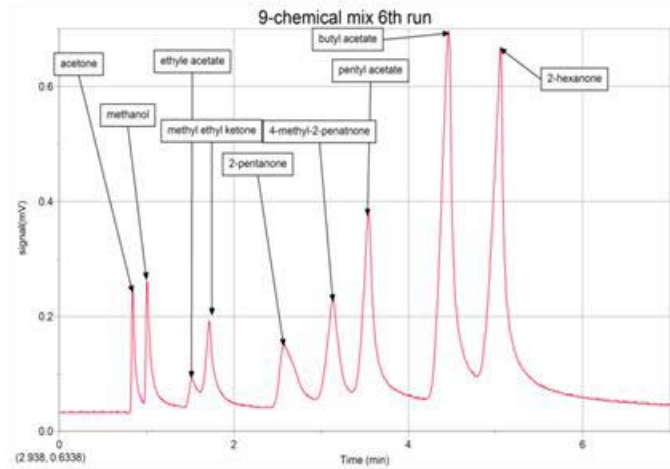


Figure 2.6 Chromatogram of Sixth Run

Best peaks were obtained from run 7 in which peaks are well separated and are sharp with high intensity. There were not many differences between the peaks from 6th and 7th run, but the intensity and sharpness is better in the 7th run. The 7th run was carried out at 7 kPa whereas 6th run was carried out at 6 kPa and at higher pressure peaks are sharper.

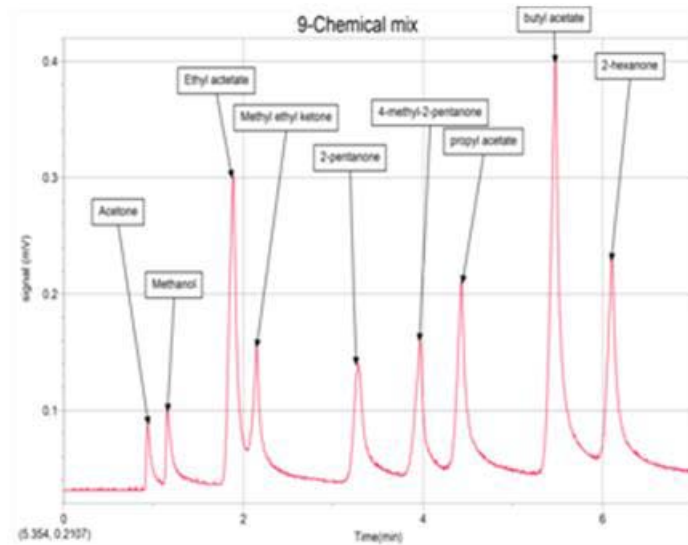


Figure 2.7 Chromatogram of Seventh Run

2.2.1.4 Conclusion

The attempt is made to design a lab for a student to be familiar with GC. Among all the temperature-pressure parameters, the parameters used in 7th run is best for separation and intensity of chemical in a mixture. In the this run the initial temperature was 35 °C, hold was 3 min, ramp was 10 °C/min, final temperature was 65 °C, final hold was 4 min, total length was 10 min, and the pressure was 7 kPa throughout the run.

2.2.2 Raoult's Law: An Experiment for General Chemistry Laboratory

The second experiment developed for undergraduate academic labs was focused on Raoult's Law. In this experiment the student uses the mini gas chromatograph as a tool to explore a concept taught in the lecture portion of the class. Below we describe a hands-on approach to study the liquid-vapor equilibrium of a binary solution containing two ketones using a bench-top gas chromatograph. This laboratory experiment utilizes chromatography to teach the concepts associated with Raoult's law.

2.2.2.1 Principle of Raoult's law

Raoult's Law is often one of the colligative properties taught as part of the general chemistry curriculum in the second semester. This law can be used to describe the relationship between the composition of a liquid and vapor at equilibrium. The mole fraction of a liquid is defined as the amount of an individual substance divided by the total amount of a substance in the mixture.

$$X_A = \frac{n_A}{n_A + n_B}$$

Equation 2.1

Where X_A is the mole fraction of substance A, n_A is the number of moles of compound A and n_B is the number of moles of compound B in the mixture.

Raoult's law states that the vapor pressure of a substance in a solution is equal to the product of its saturation vapor pressure and its mole fraction.^{1,2}

$$P_A = X_A P_A^* \quad \text{Equation 2.2}$$

Where P_A is equal to the partial pressure of component A, and P_A^* is the saturated vapor pressure of component A at the temperature of the bath and can be determined using the Antoine equation^{3,2} or by looking up values in a vapor pressure vs. temperature table.

Once the components in the solution have reached equilibrium, Dalton's law of partial pressure can be used to determine the total vapor pressure P contribution from the chemicals in the solution:

$$P = P_A + P_B \quad \text{Equation 2.3}$$

For an ideal solution, the vapor phase mole fraction⁴ is expressed mathematically as:

$$y_A = \frac{P_A}{P} \quad \text{Equation 2.4}$$

Where y_A is the vapor mole fraction of chemical component A.

In this laboratory the concepts of Raoult's Law are demonstrated experimentally with the results from the gas chromatograph and confirmed through theoretical calculations.

2.2.2.2 Experimental Procedure

Five solutions each with 2.42 g 2-butanone and varied amounts of 3-pentanone were prepared as indicated in Table 2.4. The solutions were placed in a three necked round bottom flask fitted with a condensing column and used as the basis for subsequent mixtures (see Table 2.4). A volumetric pipette was used for accurate readings. A 0.2 μL sample from each mixture was injected into the mini GC using a 1 μL syringe. Operating parameters for the mini GC were set at an initial temperature of 55 $^\circ\text{C}$, hold 2 min, ramp

10 °C/min, final temperature 80 °C with a carrier gas pressure of 7 kPa. The sample mixtures were then closed with a rubber septum that has a short length of Tygon tubing inserted through the middle. The exterior end of the tygon tubing was sealed with Parafilm and placed in a 65 °C water bath to equilibrate (see Figure 2.8). This temperature was maintained for 5 min to allow the sample to equilibrate. A 50 µL Hamilton gas-tight syringe was then inserted through the Tygon tube portion of the septum and a 30 µl vapor sample was collected from the headspace. This sample was injected into the mini GC with identical operating parameters described above. The injection procedure was repeated for each of the five mixtures. Chromatograms and peak areas were obtained using the Vernier LoggerPro software system.

Table 2.4 Mixture Concentrations. Concentrations Listed are Total Mass for Solution. Mixtures were made sequentially by adding additional aliquots of 3-pentanone to solution 1.

Mixture*	A (g)	B (g)	A Mole %	B Mole %
1	2.42	1.02	70	30
2	2.42	1.54	60	40
3	2.42	2.36	50	50
4	2.42	3.50	40	60
5	2.42	5.45	30	70

*density of (A) 2-butanone= 0.805 g/mL; density of (B) 3-pentanone= 0.813 g/mL

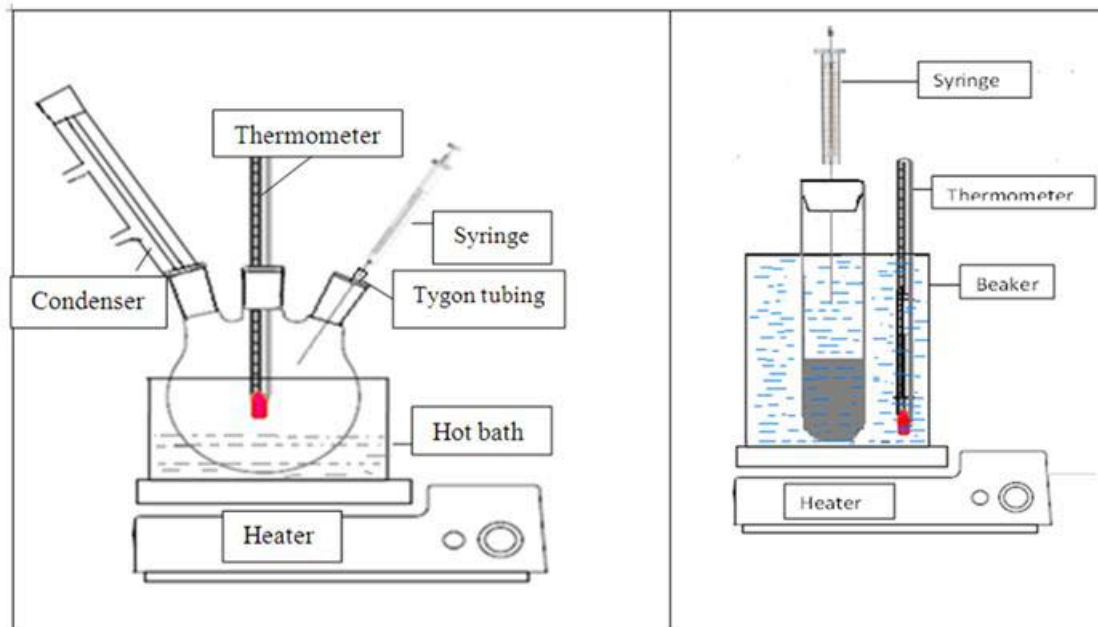


Figure 2.8 Experimental Setup using a Three-Necked Flask (left). A 15 mL Test Tube (right) can also be used with no Condenser and a Thermometer in the Water Bath.

2.2.2.3 Results and Discussion

From the series of injections 10 chromatographs are produced, each with two peaks corresponding to the chemicals in the binary mixture. The integrated areas of the peaks vary from liquid to liquid and from liquid to vapor depending on the mixture compositions. Figure set 2.9 shows some sample chromatograms.

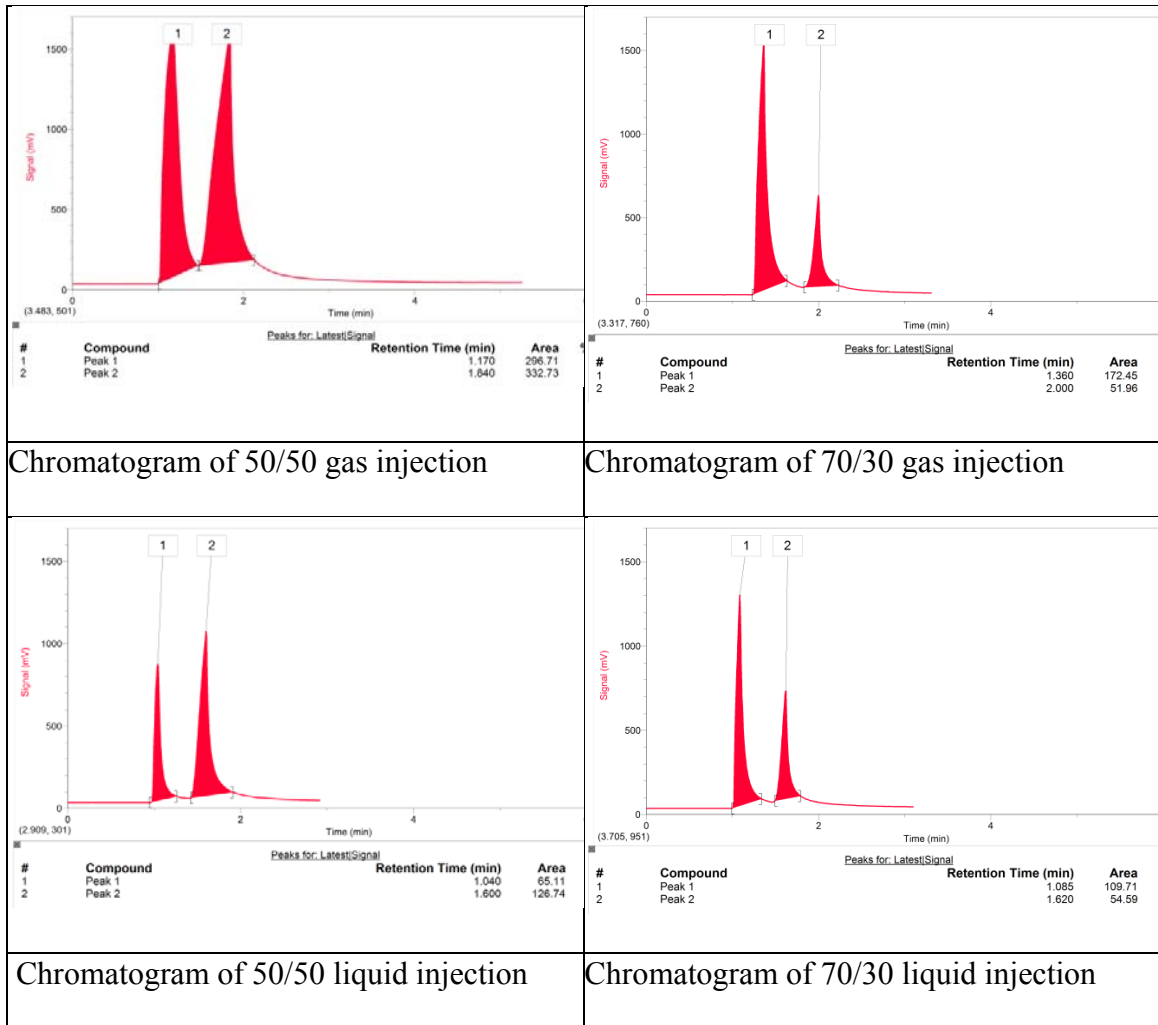


Figure 2.9 Chromatograms from Gas and Liquid Injection

Experimental data from the solution mixtures and injections of both the liquid and vapor samples is tabulated in a Table 2.5. This table contains raw data including the volume or mass of the components and the relative area of the peaks from the liquid and vapor phase chromatograms. The initial calculation was done using Equation 1 to determine mole fraction of the various mixtures (results is shown in Table 2.6).

Table 2.5 Mixture and Results from Gas Chromatographs

Mixture Number	Liquid Injection		Vapor Injection	
	%Area A	%Area B	%Area A	%Area B
1	0.804	0.196	0.939	0.061
2	0.630	0.371	0.763	0.237
3	0.300	0.700	0.688	0.313
4	0.223	0.777	0.420	0.580
5	0.029	0.972	0.167	0.834

Table 2.6 Mole Fraction of Liquid Mixtures

Mixture	Butanone (X_A)	Pentanone (X_B)
1	0.698	0.302
2	0.603	0.397
3	0.499	0.501
4	0.401	0.599
5	0.301	0.699

The Vernier mini GC detector has different sensitivity to different chemicals. To address this issue, the Vernier gas chromatograph is calibrated by injecting liquid samples of known composition. The areas obtained from these chromatographs are used to obtain a calibration curve for the gas phase data. Continuing with our data a plot of mole fraction vs. % area from the chromatographs can be found in Figure 2.10 resulting in a linear graph.

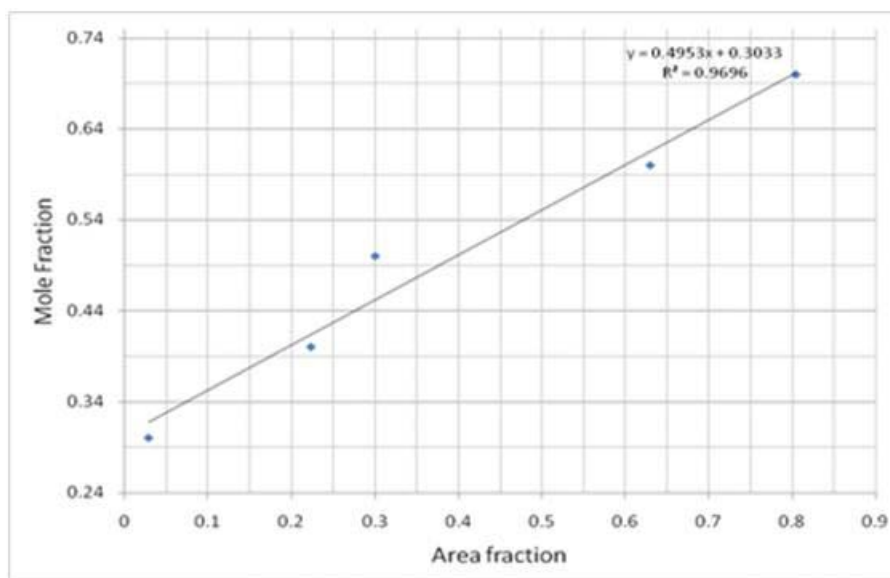


Figure 2.10 Plot of Peak Area Fraction vs Mole Fraction of 2-butanone

The equation generated from the graph is used to determine the vapor phase mole fraction from the vapor phase chromatographs. The results from our sample data can be found in Table 2.7. It can be clearly seen that these results obey Raoult's Law in that the mole fraction of the liquid (Table 2.6) is different from the mole fraction of the vapor (Table 2.7). In further calculations we will demonstrate that these differences are primarily due to differences in the saturated vapor pressure of the two chemicals in the mixture. Thus in every experiment the gas phase mole fraction of the more volatile butanone is higher in the gas phase than in the liquid phase.

Table 2.7 Vapor Phase Mole Fraction Calculated from the Chromatograph

Mixture	butanone (X_A)	pentanone (X_B)	butanone (Y_A)	pentanone (Y_B)
1	0.698	0.302	0.768	0.232
2	0.603	0.397	0.681	0.319
3	0.499	0.501	0.644	0.356
4	0.401	0.599	0.511	0.489
5	0.301	0.699	0.386	0.614

To determine the numerical mole fraction of the vapor phase the saturated vapor pressure of each component in the mixture is determined. This can be done using Antoine's equation³:

$$\text{Log}_{10} P^{\text{sat}} = \frac{A - B}{T + C}$$

Equation 2.5

Where P^{sat} is the vapor pressure, T is temperature and A , B and C are the component-specific constants.² With the use of Antoine's equation any temperature can be used for the mixtures in the controlled temperature baths.

After the saturated vapor pressure is determined⁵ the partial pressure of the mixture is calculated using Raoult's Law (equation 2). This equation will result in the partial pressure of each component in the mixture. By applying Dalton's law of partial pressures (equation 2.3) and equation 2.4, a numerical determination is made of the mole fraction of the vapor phase. The data is given in Table 2.8.

Table 2.8 Numerical Determination of the Saturated Vapor Pressure (P^*), Partial Pressures P_i , Total Pressure P and Vapor Phase Mole Fraction y_i .

P^* at 65°C 2-butanone (A) (torr)	P^* at 65°C 3-pentanone (B) (torr)	P_A (torr)	P_B (torr)	P Total (torr)	y_A	y_B
468	232	330.6	68.2	398.8	0.825	0.175
468	232	282.3	92.1	374.4	0.752	0.248
468	232	233.5	116.3	349.8	0.669	0.331
468	232	188.0	138.9	326.8	0.574	0.426
468	232	140.9	162.2	303.1	0.464	0.536

2.2.2.4 Conclusion

In addition to demonstrating the tenets of Raoult's law this exercise exposes the students to gas chromatography and gas/liquid equilibrium at varied temperatures. The small bench top chromatographs give each student hands on experience with both collection and injection of liquid and vapor samples. This approach allows the student to gain relevant experience with both equilibrium analysis and modern instrumental techniques. The Mini GC gives quantitative results for the analysis of Raoult's law. As the concentration of the 2-pentanone in the mixture is increased the corresponding peak area in the resulting chromatograph is also increased. The gas phase mole fractions obtained from the chromatographs (Table 2.7) are consistent with theoretically calculated values (Table 2.8).

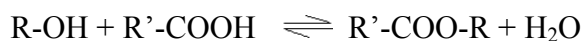
2.2.3 Verification of Esterification

2.2.3.1 Objective

Main objective of this experiment is to conduct an esterification reaction to produce ethyl acetate and to measure and analyze the GC retention time of the reactants and product involved. This is example of an organic chemistry laboratory. In addition to make student familiar with gas chromatography, it teaches concept of the esterification reaction in which ester is prepared from carboxylic acids and alcohols. This allows the student to gain experience in making new compounds by using appropriate reaction parameters such as temperature control to initiate, proceed and quench the reaction.

2.2.3.2 Introduction

It is possible to prepare esters from carboxylic acids and alcohols under acidic conditions. This is the most common method for making esters.^{6,7}



This is an equilibrium reaction therefore it is not possible to obtain a 100% yield of the ester by this method. To overcome this difficulty, a drying agent which act as surface catalyst is used along with reactants to promote product formation. This tactics have the effect of shifting the equilibrium to the right and increasing the production of ester. Ester formation can further be increased by distilling the ester out of the mixture as it is formed (the ester is often the lowest boiling member of the mixture).^{6,7}The GC parameter used for this experiment is given in table 2.9.

Table 2.9 Temperature-Pressure Profile

Start temperature	35 °C
Hold time	1 min
Ramp rate	5 °C/min
Final temperature	45 °C
Hold time	5 min
Total length	8.0 min
Pressure	3.5 kPa

2.2.3.3 Procedure

A water bath was prepared and placed on the hot plate. Temperature of the hot plate was maintained between 65-70 °C. An ice bath was also prepared to quench the reaction, therefore this is known as the quenching bath. Three test tubes were labeled and in each of these very small amount of Dowex ion- exchange resin⁸ was added which barely cover the bottom of the test tube. Its function is to act as a surface catalyst. A plastic Beral pipette was used to add 1ml (~25drops) of glacial acetic acid and ethanol to each test tube. Test tube was covered with Parafilm with a pin hole or with a loosely fitting cork stopper, for pressure release. All three test tubes were transferred to the hot water bath on the hot plate. Time was monitored and at the end of 20 min, the first test

tube was placed in ice bath and a sample collected and injected in GC. Similarly, test tube 2 and 3 were removed from hot bath, placed in ice bath at the end of 40 min and 60 min respectively, and injected in the GC.

2.2.3.4 Result and discussion

The results obtained from these three runs are given in table 2-10. Figure 2.11 is a chromatogram obtained by running the sample collected at 20 min whereas figure 2.12 and 2.13 are the chromatograms obtained by running sample collected at 40 min and 60 min respectively.

Table 2.10 Esterification Result

Sample	Retention time (min)	Peak area	Identity	% Area
Test tube 1, peak 1	1.550	74.24	Ethanol	46.45
Test tube 1, peak 2	2.290	1.00	Ethyl acetate	0.62
Test tube 1, peak 3	4.150	84.57	Acetic acid	52.92
Test tube 2, peak 1	1.580	36.87	Ethanol	16.54
Test tube 2, peak 2	2.320	4.61	Ethyl acetate	2.07
Test tube 2, peak 3	4.200	181.38	Acetic acid	81.39
Test tube 3, peak 1	1.605	28.25	Ethanol	28.74
Test tube 3, peak 2	2.385	9.83	Ethyl acetate	10.77
Test tube 3, peak 3	4.050	55.25	Acetic acid	60.49

From the data and the chromatograms it can be seen that the run at 20 min has a very small peak for ethyl acetate and the peaks for ethanol and acetic acid are large whereas the intensity and peak area of ethyl acetate has increased as the reaction progressed. This increase can be seen in chromatograms obtained from sample injected at 40 min and 60 min.

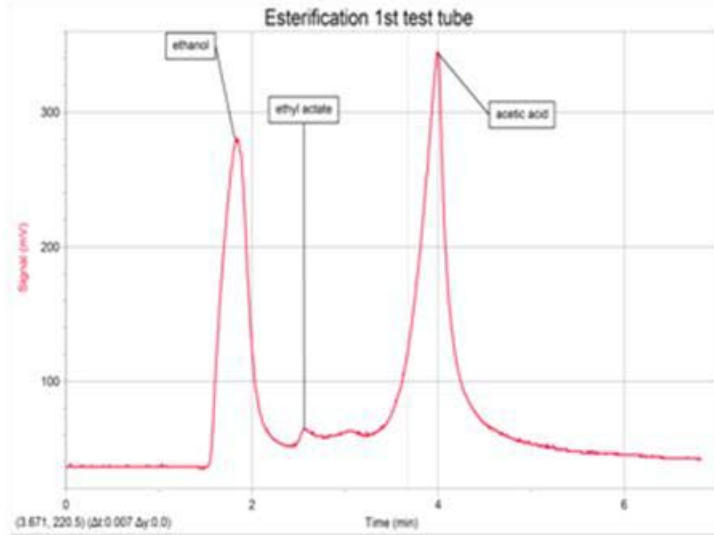


Figure 2.11 Chromatogram after 20 minutes

The reaction progressed over time and a new peak appeared at the retention time of ethyl acetate. From the data, the ethyl acetate peak was especially evident at 40 min. There was a significant difference in the peak height as the reaction progress from 40 to 60 min. At 20 min peak area of ethyl acetate was 1.00 whereas at 60 min the peak area was 28.25. The peak area of ethanol is fluctuating in all three times, this may be due to various factors; the reaction is at equilibrium and the presence of water as a product prevents the reaction from proceeding toward completion or some of the product evaporates during the reaction and is lost.

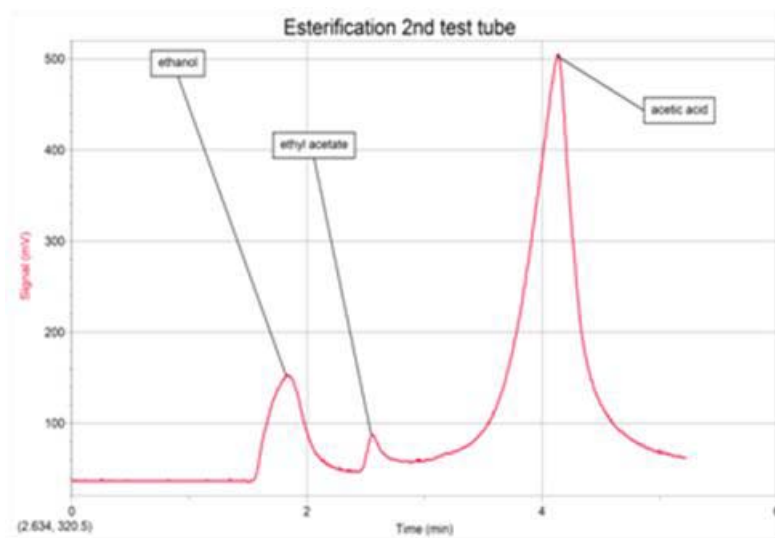


Figure 2.12 Chromatogram after 40 minutes

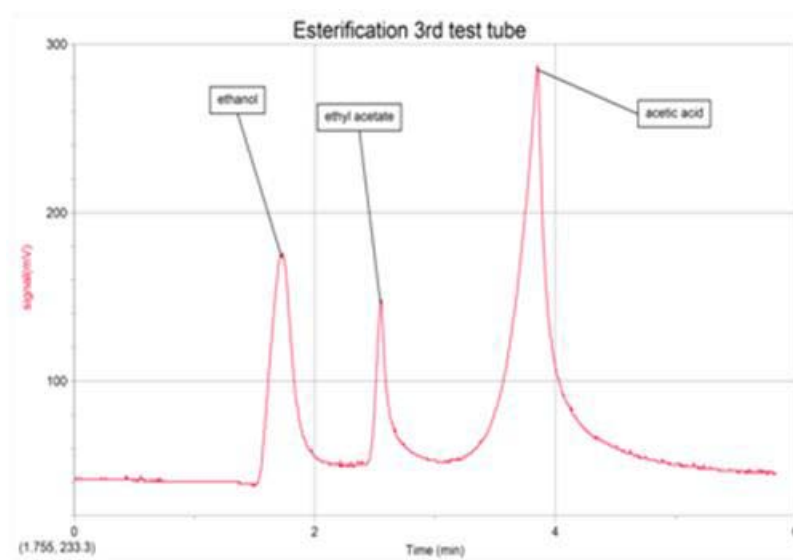


Figure 2.13 Chromatogram after 60 minutes

2.2.3.5 Conclusion

The attempt is made to understand and track the progress of an organic reaction by periodically collecting and introducing the sample in the GC. The progress in the reaction with time is easily observed in the chromatograms. As the time of the reaction is

increased, there is an increase in the amount of product formation and decrease in an intensity and peak area of reactants.

2.2.4 Fractional Distillation

2.2.4.1 Introduction

This is a process of the separation of a mixture into its component parts, or fractions, such as in separating chemical compounds by their boiling point by heating them to a temperature at which several fractions of the compound will evaporate.⁹ Schematic for distillation is shown in figure 2.14.

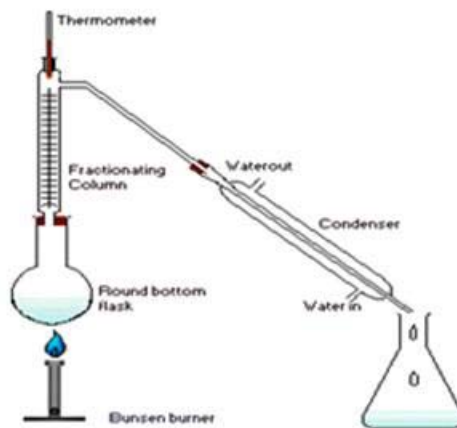


Figure 2.14 Fractional Distillation

2.2.4.2 Objective

The main objective of this experiment is to conduct the fractional distillation of a mixture of ethyl acetate and butyl acetate. Measure and analyze the retention time of the fractions and calculate the percent composition of each substance in the mixture. In addition to making student familiar with gas chromatographic process, this also helps them to understand analytical separation based on the boiling point.

2.2.4.3 Procedure

Ethyl acetate and butyl acetate were used for this experiment. Twenty ml of the ethyl acetate / butyl acetate were collected in a round-bottom flask. The flask was warmed until temperature reached the boiling point of the lowest boiling component in the mixture was reached. Three fraction of the sample were collected using three different graduated cylinders for each of the fraction. The first fraction was collected from the first drop until the temperature rose to 83 °C since boiling point of ethyl acetate is 77.1°C. A second fraction was then collected until the temperature was raised to 5 °C below the literature value boiling point (126 °C) of butyl acetate. Finally, the third fraction was collected. Each of these fractions was injected in a GC. The GC parameter for this experiment is given in table 2.11.

Table 2.11 Temperature-Pressure Profile

Start temperature	35 °C
Hold time	1 min
Ramp rate	10 °C/min
Final temperature	65 °C
Hold time	2 min
Total length	8.0 min
Pressure	7.0 kPa

2.2.4.4 Result and discussion

Initially the mixture contains 8.27% ethyl acetate and 91.70% butyl acetate by volume. Retention time and the peak area from all three fractions are given in a table 2.12. The chromatogram of the first fraction is shown in figure 2.15. The first peak is identified as ethyl acetate because the boiling point of ethyl acetate is lower than that of butyl acetate, ethyl acetate boils off first, therefore, first fraction collected contains ethyl acetate mostly as shown as in chromatogram.

Table 2.12 Analysis of the Chromatograms

Fraction	% ethyl acetate	% butyl acetate
1 st fraction	94.12	5.88
2 nd fraction	20.14	79.86
3 rd fraction	0.07	99.93

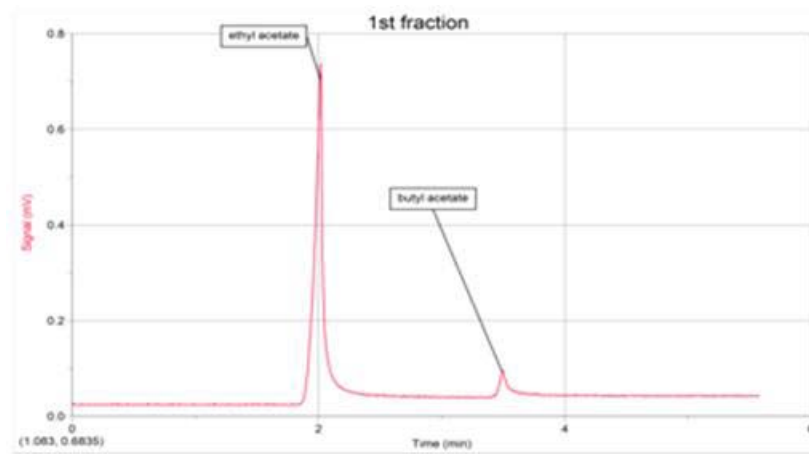


Figure 2.15 Chromatogram of First Fraction

The chromatogram from second fraction is shown in figure 2.16. This fraction was collected when the temperature of the distillation flask was between 83 °C to 121 °C, 5 °C above the boiling point of ethyl acetate and 5 °C below the boiling point of butyl acetate. Therefore, fraction contains both components of the mixture and both peaks are seen in the chromatogram.

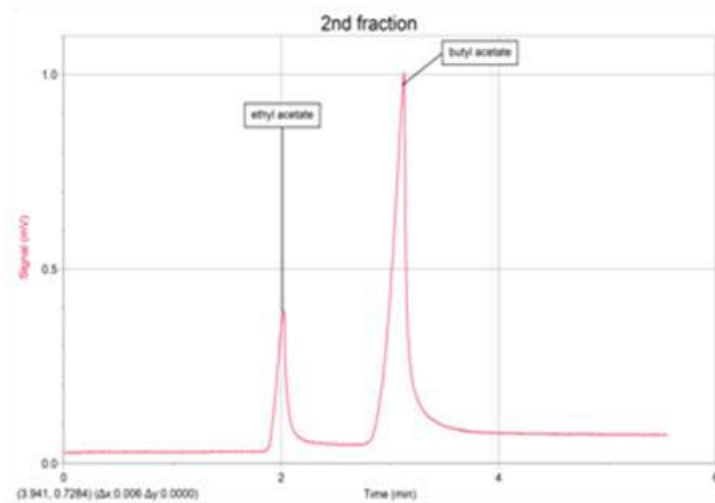


Figure 2.16 Chromatogram of Second Fraction

The chromatogram from third fraction is given in figure 2.17. This chromatogram has an intense peak with large peak area for butyl acetate whereas very small peak of ethyl acetate because this fraction was collected when the temperature was well above the boiling point of ethyl acetate and almost all ethyl acetate was already boiled off at this temperature.

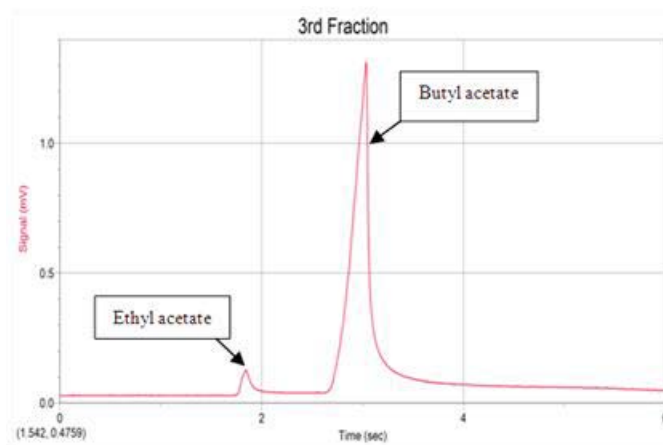


Figure 2.17 Chromatogram of Third Fraction

2.2.4.5 Conclusion

This is a general chemistry lab in which student learn about the separation of the two components in a mixture by fractional distillation process. The sample obtained from the distillation is introduced in a GC to study the extent of separation. In the first chromatogram the peak of ethyl acetate is larger than the butyl acetate which indicate the analyte with lower boiling point elute first. In the second chromatogram we can see both peaks because the sample is collected in between the boiling point of two components in the mixture and at this temperature ethyl acetate is not completely removed and butyl acetate is also present.

2.3 Summary

It is very important for undergraduate students to be familiar with analytical techniques which they may use in their career or for higher studies. Gas chromatography is considered to be one of these important techniques. Therefore, labs have been designed using a Seacoast's mini portable GC that can be included in undergraduate curriculum such as general chemistry and organic chemistry labs. The first lab entitled "Investigating Gas Chromatography" is intended to make students familiar with a GC, with opportunity to choose suitable parameters for good separation of multiple components in a sample and determine the effects of temperature programming in the GC. The second lab entitled "Raoult's Law: An Experiment for General Chemistry Laboratory" involves the study of the liquid-vapor equilibrium of a binary solution. This lab includes many calculations to make students understand the principles of Raoult's law. In this experiment, theoretical mole fraction is calculated and then it is compared with experimental mole fraction. The third lab entitled "Verification of Esterification" is designed for organic chemistry labs. This lab involves esterification reaction in which glacial acetic acid and ethanol reacts to

produce ester. The reaction is quenched at different times. The product is injected into a GC to see the reaction progress. The fourth lab entitled “Fractional Distillation” involves the fractional distillation of a mixture of ethyl acetate and butyl acetate. Three fractions are collected in three test tubes at different temperatures and injected into the GC to see the separation extent.

2.4 References

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- (4) Smith, J. M.; Ness, H. C. V.; Abbott, M. M. *Introduction to chemical engineering thermodynamics*. 7th ed.; McGraw- Hill: New York, 2004
- (5) *The constants for 2-butanone are $A=3.9894$, $B= 1150.207$ and $C=-63.904$ and for 3-pentanone $A=2.86542$, $B=716.17$ and $C=-125.978$. Using these constants with Antoine's equation at 65°C will give a vapor pressure of 468.2 torr for 2-butanone and 231.8 for 3-pentanone.*
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CHAPTER III
TESTING, EVALUATION AND APPLICATIONS OF AUTO-SAMPLING GAS
CHROMATOGRAPHY

3.1 Introduction

Gasification technologies have been used to produce fuels since the early 19th century and these technologies flourished quite well before and during the Second World War and disappeared soon after the Second World War ended since liquid fuel was easily available. Now there is renewed interest in this century old technology due to environmental concern and the increasing price of fossil fuel. Related gasification technology actually started much earlier when in 1669, Thomas Shirley conducted crude experiments with carborated hydrogen, and in 1699, when Dean Clayton obtained coal gas from pyrolytic experiments. This method became popular and the 1970's brought a renewed interest in the technology for power generation on a small scale. Since then work has concentrated on fuels other than wood and charcoal.¹

Gasification is a method for extracting energy from many different types of organic materials. Biomass gasification² is a process that converts once living organic materials into carbon monoxide and hydrogen (synthesis gas or syngas) by reacting the raw materials at high temperatures with a controlled amount of oxygen and/or steam. The syngas can be combusted directly as a methane substitute or converted into chemicals of interest.³⁻⁶ Synthesis gas primarily consists of carbon monoxide; carbon dioxide; hydrogen; nitrogen (if air is used as the oxidizing agent); methane; trace

amounts of higher hydrocarbons such as ethane and ethene; water; and contaminants such as small char particles, ash, tars, and oils. Syngas has several uses: it can be used for heat and power production by direct combustion⁷, for hydrogen production using the water gas shift reaction⁸, for the production of ammonia, methanol and Fischer-Tropsch hydrocarbons⁹, for biofuels production by anaerobic fermentation⁸, and for synthesizing dimethyl ether.^{10, 11} In contrast to fossil fuels, syngas is renewable and carbon neutral.

Intelligent control is needed to consistently control the biomass gasification process to yield a syngas composition matching downstream process needs and to prevent excessive tar levels and unwanted emissions. Most of the parameters affecting product composition can be readily controlled but the feedstock composition and moisture content are naturally variable and very difficult to measure continuously. Refinery output is highly sensitive to the naturally variable feed stock characteristics. Thus a novel method is required to control the biorefinery to improve synthesis gas production. With help of Seacoast Science Company we have developed online, real time monitoring GC technology. With further development the feedback from the GC can be used to control the biomass gasification and conversion process.

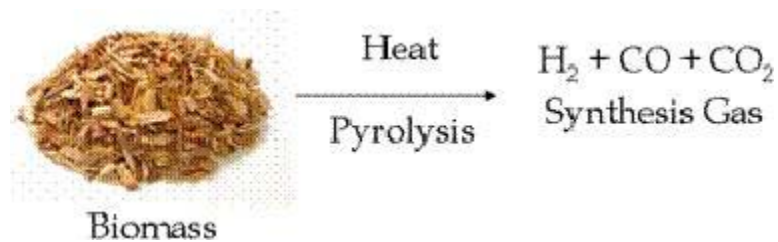


Figure 3.1 Gasification Process

3.2 Gasification principle

Drying, pyrolysis, oxidation, and reduction are the thermochemical processes that occur in every gasifier of all types and constructions.⁷ Drying of biomass occurs at temperatures above 100 °C in first zone of the gasifier reactor utilizing the heat generated from other reaction zones. Part of water vapor obtained as the result of the drying process is converted to hydrogen and the remaining appears as moisture content in syngas.⁷ Pyrolysis, the thermal breakdown of feedstock in the absence of oxygen, takes place in the temperature ranging between 200 to 600 °C, producing solid char, liquid tar and a mixture of gases. With longer residence time in this zone, the medium sized molecules and char will break down into even smaller molecules of CO, CO₂, H₂, CH₄, ethane, ethylene, and many more compounds. For shorter residence times or at lower temperature, medium sized molecules can escape and condense as tars or oils.⁷ The products formed as a result of the pyrolysis reaction enter the oxidation zone, where air (for air gasification), steam (for steam gasification) or oxygen (for oxygen gasification) is introduced and exothermic reaction occurs raising the temperature up to 1500 °C. At this stage medium-sized molecules are cracked into smaller-sized molecules like CO, H₂, CH₄, etc. Products of the oxidation zone, hot gases and glowing char enter the reduction zone, where there is insufficient oxygen for complete oxidation to occur. Thus, reduction reactions between hot gases (H₂O and CO₂) and char take place to produce CO, H₂, other constituent gases and traces of impurities; this mixture is known as syngas.⁷

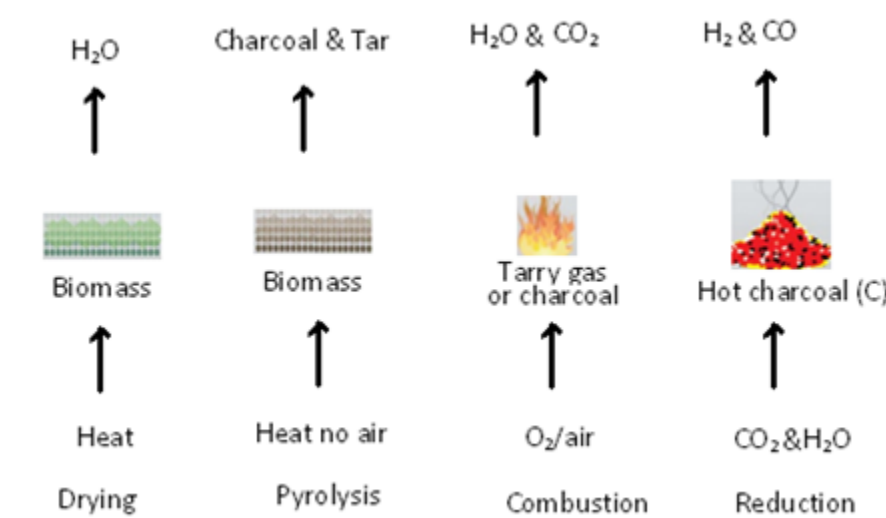


Figure 3.2 Detail in Gasification Process

3.3 Monitor System Testing

3.3.1 Experimental procedure

Two types of tests were done using auto sampling GC as listed in Table 3.1. Initially, the system was tested and calibrated using standard samples such as pure hydrogen, commercial syngas containing 48% hydrogen, 49% carbon monoxide in balance nitrogen, syngas mixed with methane, and carbon dioxide with a balance of nitrogen, mixture of hydrogen and methane in balance nitrogen. All these standard gases were purchased from Airgas Company. One-liter tedlar bags from Cel Scientific Company were used for the collection of standard samples. The collected sample was run in the auto sampling GC described in chapter 1. The standard gas was used to determine standard deviation and reproducibility of the system. The standard deviation is determined by using equation 3.1.

$$s^2 = \frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2$$

Equation 3.1

Where N is number of runs, x_i is the peak area and \bar{x} is the mean of peak area.

Table 3.1 Testing Done for the Completion of the Project

Standard sample test	Online test
Pure hydrogen	Effect of temperature in syngas production
50/50 mixture of hydrogen and carbon monoxide in nitrogen	Effect of moistened woodchips on syngas production
Mixture of hydrogen and methane in which methane concentration was varied in two run	Effect of moistened wood chips and water gas shift catalyst on syngas production
Mixture of syngas in two different concentration of methane	Effect of air flow rate (low, medium and high) in syngas production
Mixture containing syngas, methane, carbon dioxide in balance nitrogen	
Calibration of detector with hydrogen gas	

After the standard gases were tested, the GC was used for field test where biomass gasification (pine woodchips) was done using downdraft gasifier (Figure 3.3 a) from Gasifier experiments kit (GEK), CA. Some of the features of this style of gasifier is its simplicity and reliable design. In addition, the carbon conversion rate as well as conversion efficiencies are high and a relatively clean gas is produced. Syngas produced from a downdraft gasifier is clean with low a level of tars. This is an advantage of downdraft gasifiers over updraft gasifiers (Figure 3.3b).⁷ The outlet of gasifier was connected to GC by using Teflon tubing.

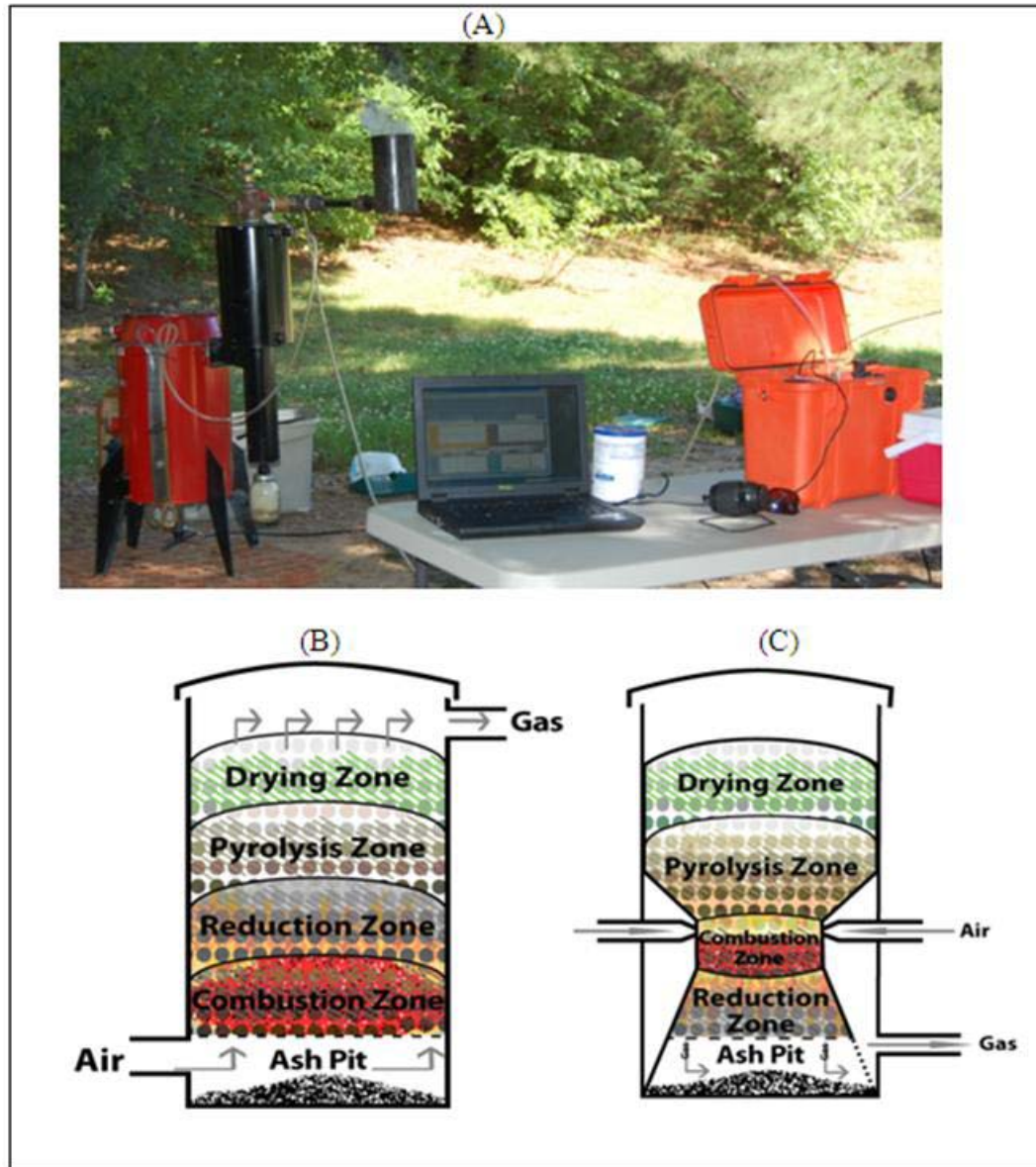
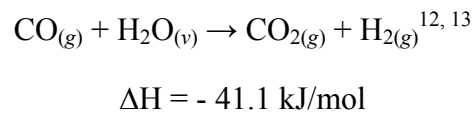


Figure 3.3 (a) Gasifier and Gas Chromatograph used in this study (b) Updraft Gasifier and (c) Downdraft Gasifier.

The gasification was done in various conditions such as by controlling the flow rate of air, introducing water gas shift reaction by passing steam to the gasifier, by moistening woodchips as shown in table 3.1. In order to blow air in to the gasifier, air pump was used. The flow rate was measured by using flow meter from Bios International Corporation, NJ. In order to monitor water gas shift reaction, the woodchips were

moistened before feeding into the gasifier. Even the temperature was monitored throughout the gasification process to see the effect of temperature in production of syngas. Thus, the sensitivity of the MOS is determined with respects to variations in gasifier operating conditions. Various conditions gave various results. For example, an increase in temperature increases carbon monoxide, introducing water during gasification in a gasifier promoted the water gas shift reaction increasing the hydrogen concentration. The result obtained by using moistened woodchips is consistent with the water gas shift reaction where the percentage of hydrogen increases with moisture content. The water gas shift reaction is as follows:



3.4 Result and discussion

3.4.1 Test using standard samples

3.4.1.1 Pure hydrogen test

Extensive system testing was conducted using the auto sampling GC described in chapter I. The sample was collected in a tedlar bag and connected to the autosampling GC. Figure 3.4 shows sample chromatograms of the pure hydrogen. The peak area, standard deviation and relative standard deviation is given in table 3.2. As described in chapter 1, the auto sampling GC was set to collect and inject sample. Total length of the run was 2200 seconds. During this run, sample was injected 7 times. The first peak appeared at 30 sec after the run was started. MOS sensors measure the change in resistance when analyte interact with detector. The resistance values measured by the MOS sensors are converted to a voltage value between 0 and 5 V in the electronics.

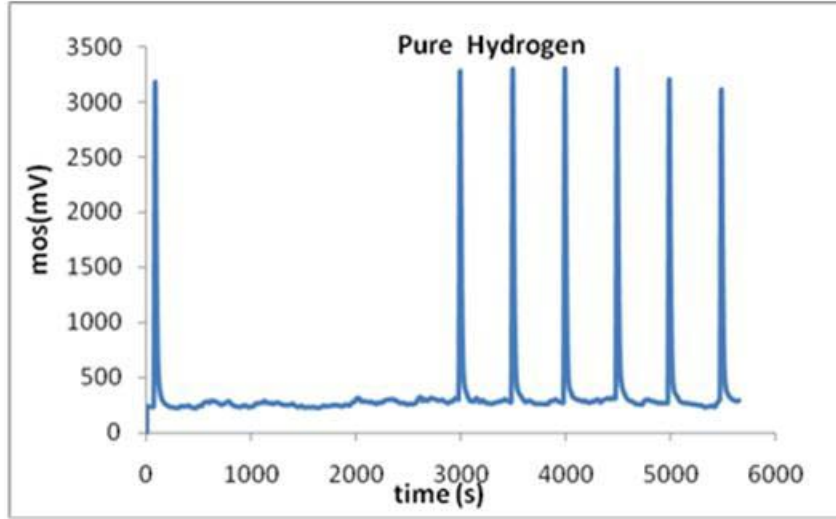


Figure 3.4 Chromatogram of Pure Hydrogen

Table 3.2 Peak Areas of Hydrogen in Various Run

Run	1 st	2 nd	3 rd	4 th	5 th	Standard deviation	Relative standard deviation
Peak area	60912	61777	62802	61381	61719	696.7	1.12

3.4.1.2 Hydrogen and carbon monoxide mix test

The standard gas mixture for these tests contained 50 % hydrogen and 50% carbon monoxide. Even though it is a 50% mixture, in a chromatograms the peak intensity of hydrogen is significantly higher than that of carbon monoxide. Data is shown in table 3.3 and chromatogram is given in figure 3.5.

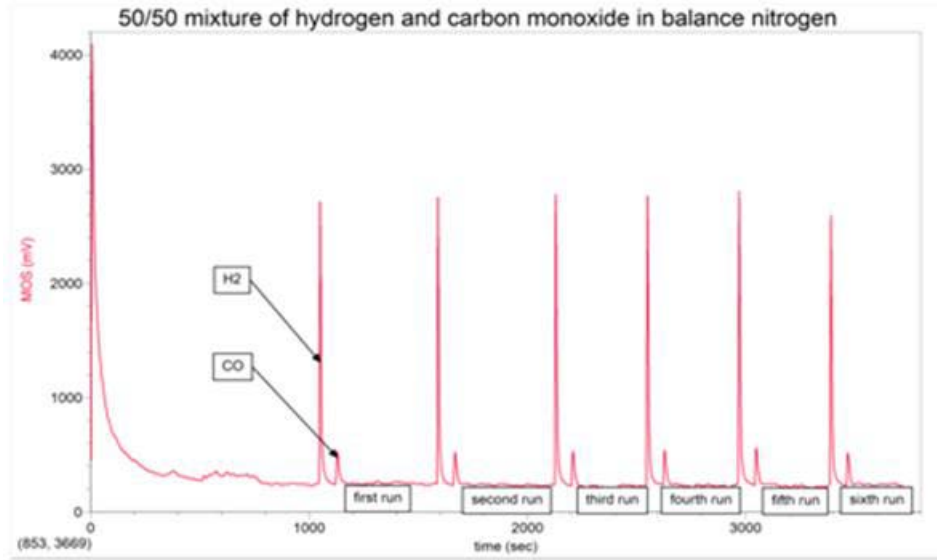


Figure 3.5 50 /50 Hydrogen and Carbon monoxide Mix

Table 3.3 Peak Area Percentage Ratio of H₂ and CO in a Total Volume of Gas for 50/50 Mix of H₂ and CO

Injection	H ₂ peak area	CO peak area	Area percentage ratio of H ₂	Area percentage ratio of CO
1 st	56924	6235	90	10
2 nd	59404	6114	91	9
3 rd	57395	5976	91	9
4 th	56493	4431	93	7
average	57554	5689	91	9

3.4.1.3 Test using various concentration of hydrogen and methane

Next, the concentrations of the individual gases were varied to determine if the MOS would show a change in response magnitude. Figure 3-6 shows six consecutive injection of mixture of hydrogen and methane. A sample for first three injections contains 0.8% hydrogen and 1.5% methane in balance nitrogen whereas for last three injections the methane concentration was increased to 3.5%. The response of the MOS to the methane is fairly consistent at each concentration and an increase in peak height is

clearly observed as the concentration is increased. This test was run with nitrogen as the balance of the sample gas, and with 40 psi air as the carrier, giving a flow of approximately 10 ml/min.

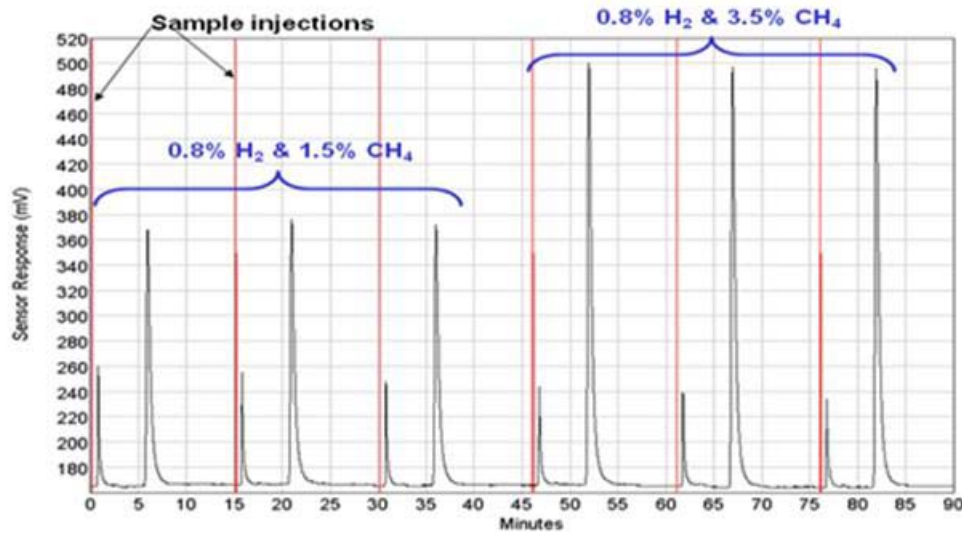


Figure 3.6 Metal-Oxide Detector Output for Hydrogen and Methane Mixture

3.4.1.4 Test using mix 20% hydrogen, 20% carbon monoxide, 5% methane, 20% carbon dioxide and 35% nitrogen

Next, three gases, all detectable by the MOS were mixed together to determine the success of separation. Figure 3-7 shows sample chromatograms of 20% hydrogen, 20% carbon monoxide and 5% methane, 20% carbon dioxide and 35% methane. The retention times for hydrogen, carbon monoxide and methane is given in table 3.4. Table 3-5 contains the average peak retention times and heights for the minimum concentrations in a fuel gas mix. The carbon monoxide peak appeared before the methane peak because the molecular size of carbon monoxide is smaller than that of methane. The boiling point of carbon monoxide is -191.5°C where as that of methane is -161.6°C . This may be another cause for the carbon monoxide to elute before methane.

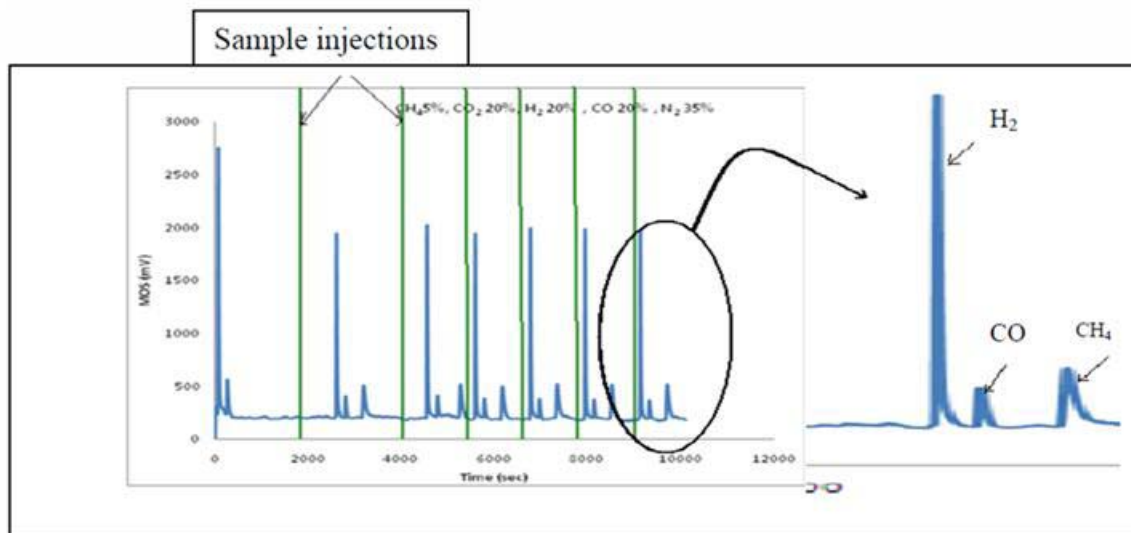


Figure 3.7 MOS Output for Hydrogen, Carbon Monoxide and Methane Mixture

Table 3.4 Retention Times of a Fuel Gas Mix

Injection	1 st peak (s) (H ₂)	2 nd peak (s) (CO)	3 rd peak(s) (CH ₄)
1	29	105	255
2	30	107	256
3	30	105	256
4	28	106	254
5	28	106	254
6	29	106	255

Table 3.5 Average Peak Retention Times and Heights for the Minimum Concentrations in a Fuel Gas Mix

Chemical	# of Samples	Retention time (s)		Height (mV)	
		Avg	Std. Dev	Avg	Std. Dev
20% H ₂	6	29	0.89	1975	32.71
20% CO	6	106	0.77	343.3	5.16
5% CH ₄	6	255	0.89	507.5	4.18

Next the concentrations of the individual gases within the mix were varied.

Figure 3.8 is an overlay of six consecutive samples of a mix of 8% H₂, 18%CO and CH₄ in Nitrogen. Three samples have 1%CH₄, and three have 3.5% CH₄. The graph shows clear separation, precise elution times, reproducible peak heights, and a clear increase in response magnitude with increased CH₄ concentration.

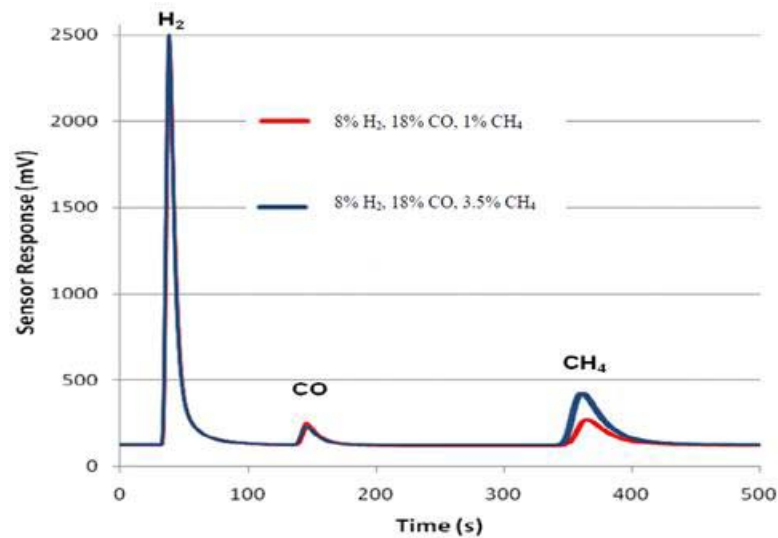


Figure 3.8 Separation of H₂, CO₂ and CH₄ with CH₄ Concentration Varied

3.4.1.5 Calibration with hydrogen

The detector used in the auto sampling GC has different sensitivities for different gases. To address this issue, the gas chromatograph is calibrated by injecting the hydrogen gas known composition in a balance nitrogen. The areas obtained from these chromatographs are used to obtain a calibration curve as shown in figure 3.9. The calibration curve is non-linear. The MOS detector can produce linear response only for very low analyte concentration whereas non-linear for higher concentration. The calibration curve obtained from various concentration of hydrogen is used to determine the amount of hydrogen from the gasification process.

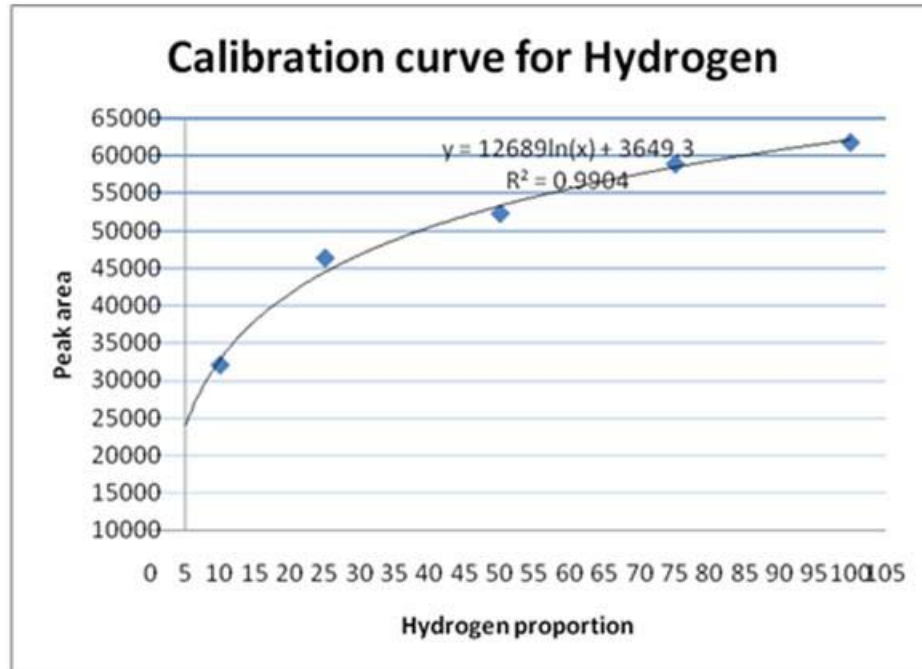


Figure 3.9 Calibration Curve for Hydrogen

3.4.2 Online monitoring

Syngas produced by gasification of wood chips was carried out in the down draft gasifier described above. Two types of pine woodchips were used in terms of moisture content originally; 7.9% and 10.3% by mass. Some tests were carried out using the wood chips containing 7.9% moisture whereas others were carried out using woodchips with 10.3% moisture content. Various conditions were used for the gasification. A change in gasification conditions will result in different ratio of hydrogen to carbon monoxide production. The conditions used for gasification and its effect on production of syngas are described below.

3.4.2.1 Effect of temperature in syngas production

First, the test was carried out using the original woodchips containing 10.3% moisture by mass. The effect of temperature was measured varying temperature from

400 °C to 705 °C. As the temperature increases production of syngas increases respectively. Figure 3.10 and table 3.6 gives the effect of temperature on syngas production.

Table 3.6 Effect of Temperature on the Syngas Production

Run	Temp(°C)	Peak area H ₂	Peak area CO	% area H ₂	% area CO
1 st	409	30963	1937	94	6
2 nd	601	41591	4703	90	10
3 rd	606	41819	3398	92	8
4 th	703	42498	2629	94	6
5 th	563	38553	2052	95	5
6 th	548	34735	1504	96	4

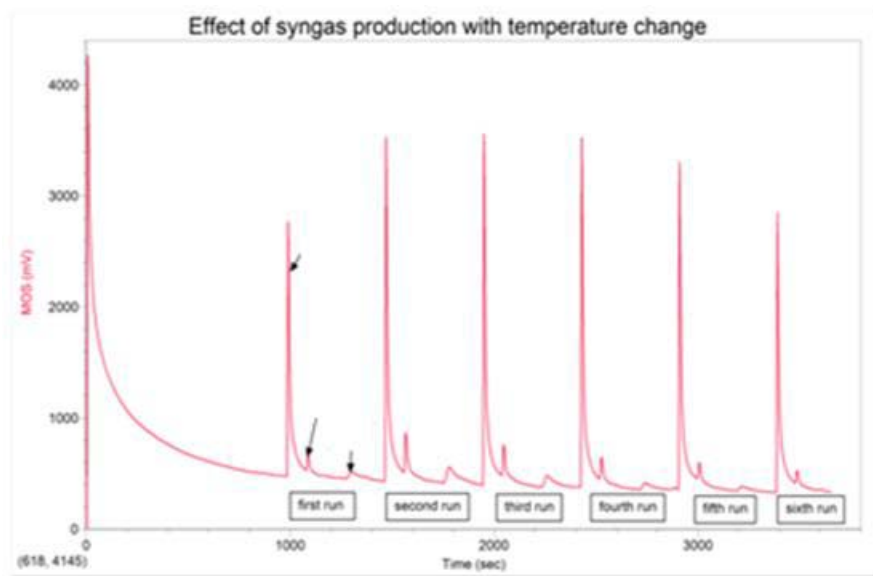


Figure 3.10 Effect of Temperature on Peak Intensity and Area

3.4.2.2 Effect of water gas shift reaction

To monitor the effect of the water gas shift reaction on the hydrogen to carbon monoxide ratio the gasification of woodchips containing 7.9% moisture by mass was done. For the first run woodchips were gasified without changing any gasifier conditions

during the run. For the second run, the water gas shift reaction was promoted by increasing the moisture content of the woodchips and by addition of steam to the gasifier while it was operating. This caused a corresponding increase in the % area of the hydrogen when compared to the results obtained from the gasifier without a steam supply. The water gas shift reaction was used to increase the ratio of hydrogen to carbon monoxide. This is caused by the reduction of the steam in the reduction zone.¹⁴ Even though the production of hydrogen was increased as the steam was introduced in the gasification process, there is not a large difference between the gasification with steam and without introduction of steam. This must be due to the temperature inside the gasifier (or only moderate increases in humidity). At lower temperature, the production of carbon monoxide is higher relative to hydrogen. We found that the production of hydrogen increased with increasing reactor temperature. Other factors that influences this result must be steam to biomass ratio,¹⁵ the steam/air ratio may be not high enough to bring a sufficient change in hydrogen production. The method we used for the steam introduction may be not an efficient to bring large change in hydrogen production. Finally, initial testing of the water gas shift reaction catalyst (copper based) was used in the gasifier during biomass gasification. The 30 g of catalyst was placed in a reduction zone as shown in figure 3-11a. This caused a large change in peak height, area, and a small change in the percentage ratio between hydrogen and carbon monoxide compared to the run without catalyst. The chromatogram and result is given below in figure 3-12 and table 3-7 respectively. In addition to syngas peaks there are few other peaks. Other peaks are for hydrocarbons such as ethylene, ethane which are produced during gasification process.

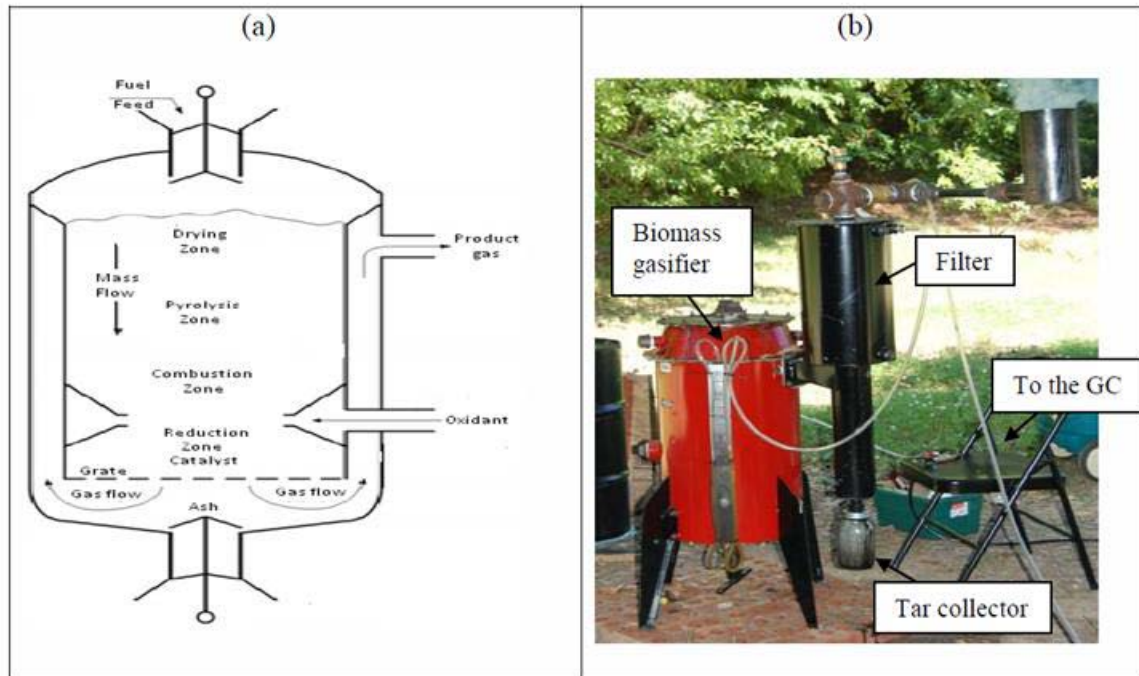


Figure 3.11 (a) Systematic of Gasification Process and (b) The Gasifier for this Project

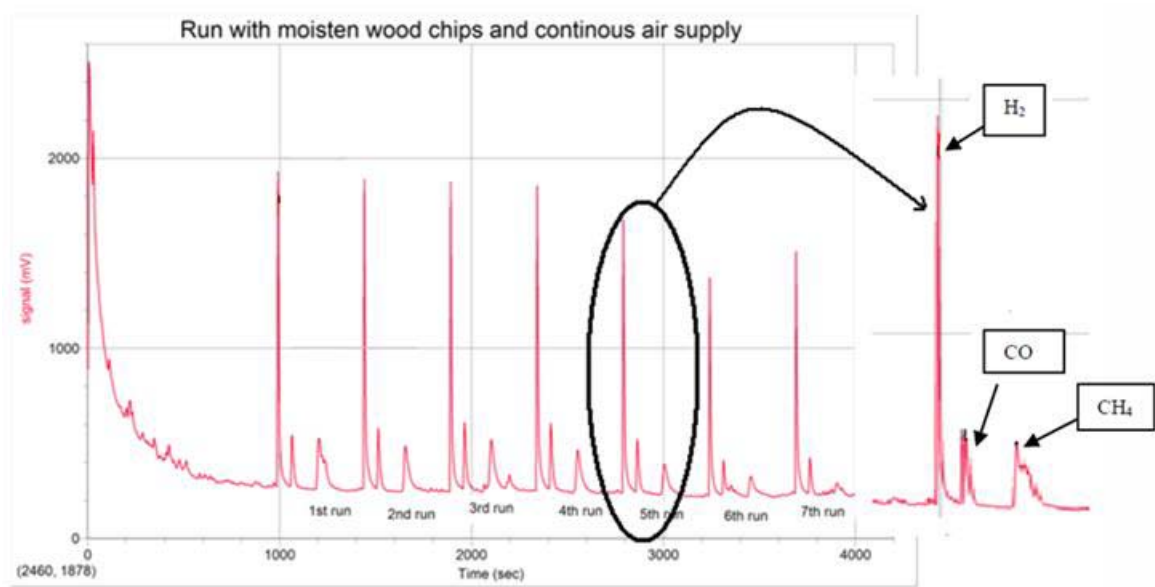


Figure 3.12 MOS Response when Moistened Woodchips Are Used and Air Flow Rate is Maintained Between 30-32 L/min.

Table 3.7 Percentage Ratio of Hydrogen and Carbon Monoxide Obtained from the Gasifier at Various Conditions. (With the introduction of steam and by using water gas shift reaction the hydrogen concentration relatively increased and carbon monoxide concentration is relatively decreased.)

# of run	Area % with air		Area % with woodchips and steam		Area % with woodchips, steam and catalyst	
	Hydrogen	Carbon monoxide	Hydrogen	Carbon monoxide	Hydrogen	Carbon monoxide
1 st run	82.0	18.0	84.8	15.3	93.4	6.6
2 nd run	85.4	14.6	86.6	13.4	93.9	6.7
3 rd run	83.8	16.2	89.6	10.4	94.1	6.0
4 th run	84.8	15.2	89.4	10.6	92.9	7.1
5 th run	86.9	13.1	94.4	5.6	93.5	6.5
6 th run	82.9	17.1	91.9	8.2	94.3	5.7
7 th run			87.6	12.4	94.2	5.8
Average area percentage	84.3	15.7	89.2	10.8	93.7	6.3
Standard deviation	1.77	1.77	3.47	3.48	0.50	0.50

It is found that with the application of water and WGS catalyst there is an increase in the hydrogen yield. The results obtained from these processes are compared to that of standard gas test. The peak area ratios of hydrogen to carbon monoxide from these runs were compared with the peak area ratio of 50/50 standard syngas mixture as shown in following histograms (figure 3.13 for hydrogen and figure 3.14 for carbon monoxide). The peak area ratio of hydrogen to carbon monoxide for 50/50 mix standard syngas is 91:8 percent. From the histograms below it is observed that ratio of hydrogen to carbon monoxide obtained from moisten woodchips is slightly lower than that of 50/50 mix whereas by using catalyst along with moisten woodchips the ratio of hydrogen to carbon monoxide is more than that of standard sample.

The result obtained from these three conditions was statistically tested using t-test to determine if a difference exists in between the results. A two sample test was

conducted between average area percentages from simple gasification run and moistened woodchips gasification and between average area percentages from moistened woodchips gasification and moistened woodchips gasification in presence of catalyst. T-test values obtained from t-calculation are below 0.05 and it indicate that our result is relevant and within 95% confidence interval. An F-test was also conducted to determine if there is difference in the variance. From the F-test it was found that the f calculated is approximately same as that of F-table value which shows that the results obtained from these runs belong to same population variances.

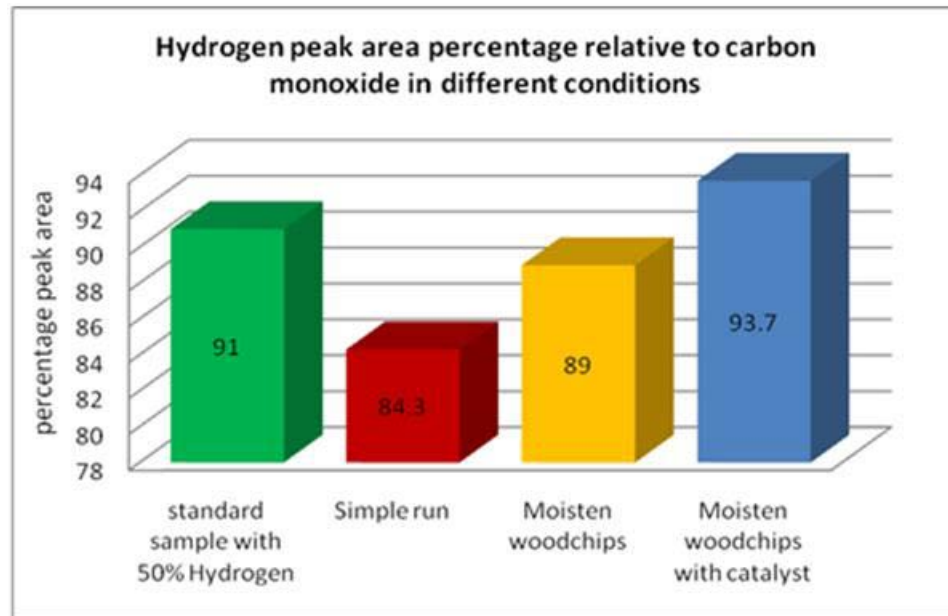


Figure 3.13 Peak Area Percentage of Hydrogen Relative to Carbon Monoxide from Gasification and Standard Sample.

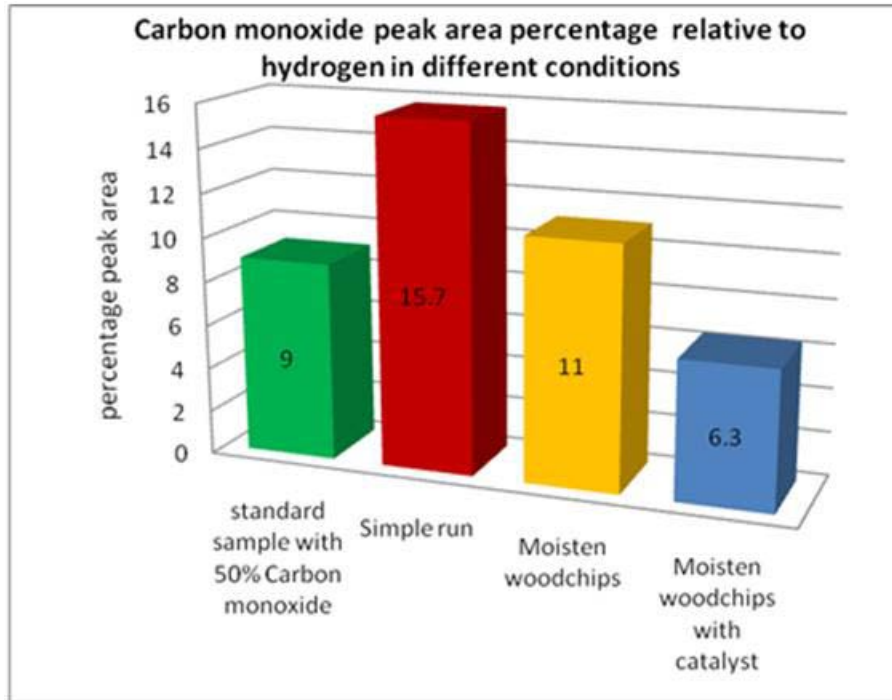


Figure 3.14 Peak Area Percentage Carbon Monoxide Relative to Hydrogen from Gasification and Standard Sample

3.4.2.3 Effect of air flow in the production of syngas

Air flow rate also affect the production of fuel gas¹⁶⁻¹⁸ as given in the table 3.9.

The air flow rate was also monitored during the gasification process. Woodchips containing 10.3% moisture was used for this part of work. Three different flow rates were maintained for three batch gasification runs. The low flow rate was maintained between 1-2 l/min, medium flow rate was between 10-12 l/min and the high flow rate was between 27.5-29.5 l/min. Figure 3.15 and 3.16 are the chromatograms obtained in a controlled flow rate. Even though there is no difference in the percentage ratio of hydrogen and carbon monoxide among various flow rate of air, there is increase in the peak area of both hydrogen and carbon monoxide with increase in flow rate. The result is given in table 3-9.

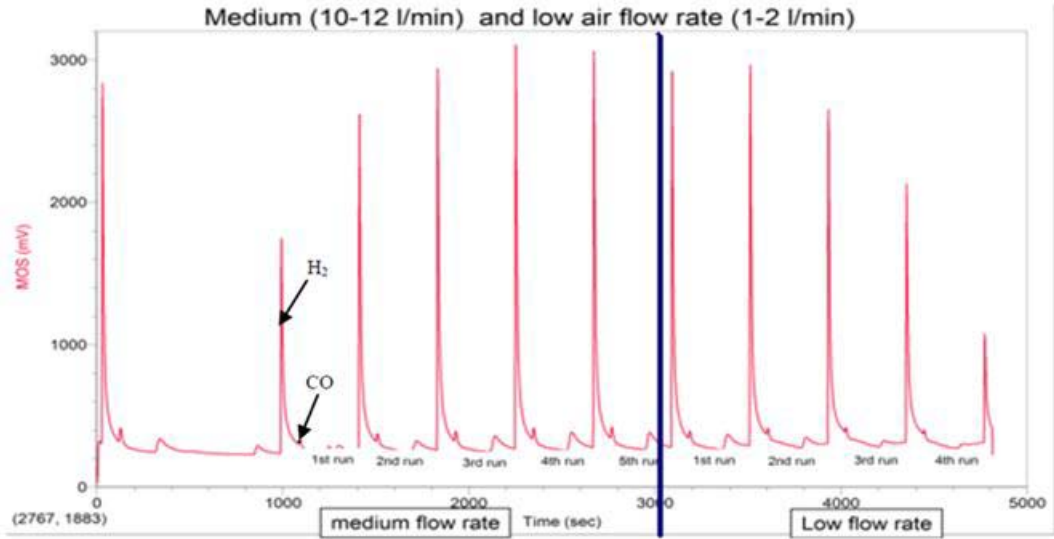


Figure 3.15 MOS Response to Syngas from Moistened Woodchips and Air Flow Rate 10-12 l/min and 1-2 l/min

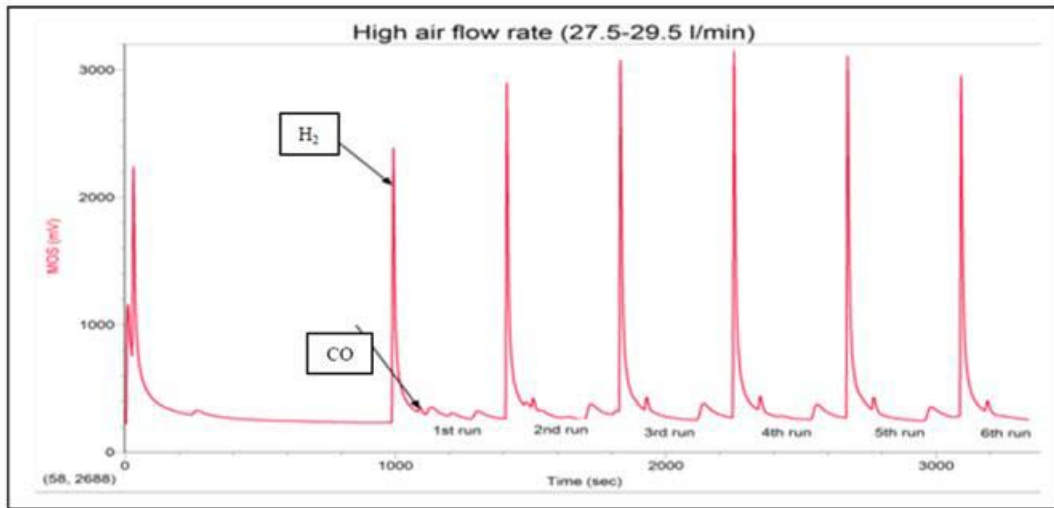


Figure 3.16 MOS Response to Syngas from Moistened Woodchips and Air Flow Rate 27.5-29.5 l/min

Table 3.8 Peak Area of Hydrogen and Carbon Monoxide in Three Different Air Flow Rates.

# of run	Area at low flow rate (1-2 l/min)		Area at medium flow rate (10-12 l/min)		Area at high flow rate (27.5-29.5 l/min)	
	Hydrogen	Carbon monoxide	Hydrogen	Carbon monoxide	Hydrogen	Carbon monoxide
1 st run	24795	109	31509	777	34379	1210
2 nd run	33176	617	35282	923	37089	1293
3 rd run	31818	493	34382	865	38232	1216
4 th run	32212	394	35669	1041	34232	1055
Average	30500	403	34211	902	35983	1194
Standard deviation	3846	216.3	1879.9	110.7	1993.3	99.7

The results obtained by using the different air flow rate is compared to calibration curve obtained from the various know composition of hydrogen. From the peak area it is found that at low flow rate the hydrogen percentage in gas from gasification is below 10 % of total composition. When the flow rate is between 10-12 l/min, the hydrogen percentage is around 10%. When the flow rate increases to 27.5-29.5 l/min, the hydrogen percentage in the entire composition goes between 16-18%.

The results obtained from effect of air flow rate were also evaluated statistically. A two sample t-test was conducted in Excel between results obtained from low flow rate and medium flow rate of air, and between the results obtained medium flow rate and high flow rate. T-test values obtained from t-calculation are shown in table 3.9.

Table 3.9 Statistical Test of the Result Obtained Using Low, Medium and High Flow Rate of Air During Gasification

Variables	T-test values
Between area of H ₂ using low flow rate and medium flow rate	0.15
Between area of H ₂ using medium flow rate and high flow rate	0.24
Between area of CO using low flow rate and medium flow rate	0.01
Between average area of CO using medium flow rate and high flow rate	0.00

The t-calculated results for H₂ between low flow rate and medium flow rate and between medium flow rate and high flow rate are above 0.05 which shows that increase in H₂ at various flow rates is not within 95% confidence interval. The t calculated values for CO between low flow rate and medium flow rate and between medium flow rate and high flow rate are below 0.05. These t-test results show that there is no statistical difference between the hydrogen productions at three different flow rates whereas there is a difference in the production of carbon monoxide at above mentioned three flow rates. Therefore, increase in syngas production with increase in flow rate is mainly due to increase in CO concentration, statistically. F-test was also conducted to determine if there is difference in the variance. From the F-test it was found that the F calculated is approximately same as F-table value which shows that the results obtained from these runs belong to same population variances.

3.5 Conclusion

Temperature affects the yield of syngas gas. Increasing the reactor temperature increases the syngas yield. A water gas shift catalyst can be used to increase the hydrogen to carbon monoxide ratio.¹⁹ In our limited study we did see that the use of the WGS catalyst did result in increase of hydrogen to carbon monoxide ratio. There are some

reasons for low yield of hydrogen such as the temperature inside the gasifier was not high. At temperature higher than 900 °C, the hydrogen production is increases.²⁰ The maximum temperature in our gasifier was between 800 °C 900 °C. At lower temperature the production of carbon monoxide is higher compared to the hydrogen and production of hydrogen increased with increase in temperature. Other factors that influence this result must be steam to biomass ratio.¹⁵ The method we used may not be adequate to result in a significant change in hydrogen production. Another factor that influences the production of syngas from gasification is airflow rate. The yield of fuel gas is increased by increase in the flow rate of air.

3.6 Summary

Our prototype GC has been used successfully for monitoring the concentration of gases in a fuel gas mix. The GC was calibrated with standard samples having various compositions. These tests help to determine the sensitivity of MOS and to calibrate GC. The GC has been used successfully to monitor the gases from gasification at various conditions. Different conditions used in gasification to produce different ratio of hydrogen to carbon monoxide. Therefore, with further development our GC can be used for real time feedback control of gasification of biomass to produce a range of different biofuels such as diesel, petrol, jet fuel etc. The feedback obtained from gasification of biomass in real time can be used for the optimizing gasification process for syngas production in right proportion for specific biofuel production.

3.7 References

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CHAPTER IV

CONCLUSION

The focus of my work is on the development of portable analytical instruments, specifically miniature gas chromatographs, and their applications. Two prototypes GCs were developed and tested as part of this thesis including a miniature GC and a portable auto sampling GC. The miniature GC does not have a large oven instead utilizes resistive heating to raise the temperature of the column and a MEMS chemicapacitive detection system for detection of volatile organic compounds. A small pump pulls ambient air through the system; avoiding the requirement of compressed gas cylinder.

The mini GC was designed specifically for low cost and user friendly operation in an academic teaching laboratory and can be used for both quantitative and qualitative analysis. The range of detection capabilities is limited when compared to bench top GC's. As a general rule it can be used for organic compounds with boiling points from 20°C to 200°C. This instrument has been design for training today's student on how to use modern instrumentation. Several new labs have been successfully developed including those that teach the separation and quantification with chromatography, Raoult's Law and oxidation of an alcohol into a ketone along with the concepts that they are designed to teach the student. The small bench top chromatograph gives each student hands on experience with both collection and injection of liquid and vapor samples. This approach allows the student to gain relevant experience with both equilibrium analysis and modern instrumental techniques. In addition to demonstrating theories of distillation,

esterification and the tenets of Raoult's law this exercise exposes the students to gas chromatography and gas/liquid equilibrium at varied temperatures.

The portable auto sampling GC has been used for detection of combustible gases for real time chemical monitoring. This GC includes the same components as most conventional gas chromatographs with the addition of an automatic gas sampling loop. It has been successfully used for the standard sample detection in the laboratory for calibration and for online detection in the field. The portable auto sampling GC has been successfully used for monitoring combustible gases such as hydrogen, carbon monoxide and methane as an important first step for controlling the system. The real time monitoring property of the system can be used for feedback control of gasification for the production of bio-fuel from biomass with further development. Intelligent control is needed to consistently control the biomass gasification process to yield a syngas composition matching downstream process needs and prevent excessive tar levels and unwanted emissions. Depending upon the type of biofuel the gasification process can be modified to produce the correct proportion of hydrogen, carbon monoxide and methane.

Modification of our existing auto-sampling is other goal that will be a focus in future work. Since our auto-sampling GC cannot separate and detect volatile organic compounds, installation of a second column that will not absorb water and is suitable for volatile organic separation will be our other target. The GC will be modified to heat this second column. This modification will allow detection of a wider range of chemicals and aid in separation and identification of the trace carbon containing compounds produced during biomass gasification.