

CHAPTER 1

INTRODUCTION

1.1 Overview

Environmental and political problems created by our dependence on fossil fuels combined with diminishing petroleum resources are causing our society to search for new renewable sources of energy and chemicals. Apart from that, the awareness of global warming issues has created an importance on obtaining alternative fuels and energy from bio sources. Nowadays, various alternative fuels such as hydrogen, ethanol and bio-diesel are being used to fulfill the energy requirement.

Bio-diesel has become an attractive renewable and alternative fuel because of its environmental impacts such as net zero carbon monoxide emission and no or less emission of SO_x and NO_x (Valliyappan, 2008). There are four ways to produce bio-diesel which are direct use and blending, micro emulsions, thermal cracking (pyrolysis) and transesterification (Ma and Hanna, 1999). Transesterification of oil and fats is the common method used in producing biodiesel because other methods affect the engine performance by producing carbon (Valliyappan, 2005). Malaysia is one of the largest sources of palm oil in the world. Thus, there is a great development potential of using biodiesel as an alternative fuel produced from palm oil as a feedstock in transesterification. In addition, nowadays as the price of fossil fuel increases drastically, an alternative fuel is the most suitable and more economical option to be chosen by users worldwide.

Glycerol is the main by-product in the biodiesel industry (via transesterification of vegetable oil). It has been regarded as a promising source for future bio refineries because it can be converted to various derivatives used in fuels, chemical, automotive, pharmaceutical and detergent (Pagliaro 2007). 10 wt% of glycerol will be produced in the transesterification process of bio-diesel. This means that in every 1 tonne of bio-

diesel that is manufactured, 100kg of glycerol are produced as a by-product for the process (Peterson et al, 2006).

In a worldwide, the demand for bio-diesel has increased and resulting a large quantity of glycerol produced throughout the huge production of biodiesel. This leads to the price decreasing of glycerol because it was said that glycerol markets are very limited for a low grade quality of glycerol produced from the production of biodiesel.

To treat and refine crude glycerol for purification is not suitable for a small to medium sized plants when money is taken into consideration. In order to overcome this problem, the glycerol should be brought into play in any possible way which can give benefits and cost effective to the users. From the previous study, it is noted that conversion of glycerol to hydrogen became an attractive solution as hydrogen has a big potential to be a future clean and renewable energy source especially for fuel cell and it also can be stored as a chemical feed stock.

1.2 Objectives and Scope of Study

The main objective of this research is to carry out study on optimization of hydrogen production from aqua reforming of glycerol. The project deals mainly with thermal degradation process in a presence of catalyst.

The specific objectives are :

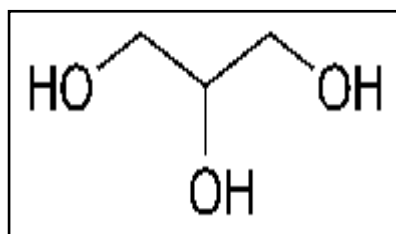
- To investigate the optimum process variable which include the effects of temperature and concentration of catalyst for the APR process.
- To quantify gas analysis for the effluent gas from the APR process.

CHAPTER 2

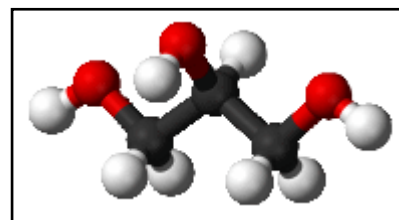
LITERATURE REVIEW

2.1 Glycerol

Glycerol, also refer as glycerin is a colorless, odorless, sweet tasting, and viscous liquid widely used in pharmaceutical formulation, cosmetic and food products. It is a liquid by-product of biodiesel production and can naturally found in the cells of plants, animals and humans. The melting point of glycerol is at 17.8 °C and it boils to decompose at 290 °C. Glycerol is a liquid organic compound of the alcohol family. The chemical formula of glycerol is HOCH₂CHOHCH₂OH (C₃H₅(OH)₃). Glycerol has three hydrophilic alcoholic hydroxyl groups that are responsible for its solubility in water and its hygroscopic (absorbs water from the air) nature.



(a) Glycerol



(b) Ball-and-stick model for glycerol

glycerol

Figure 2.1 : Three hydroxyl group in glycerol and ball-and-stick model for glycerol

2.2 Synthesis Gas (Syngas)

Syngas is an acronym of synthesis gas. Syngas is created via a thermochemical conversion. Syngas can be used in place of natural gas or changed it to make bio-fuel and others chemical products. Syngas is made up of varying amount of carbon monoxide and hydrogen.

There are many methods can be used in producing syngas. One of the methods is Aqueous Phase Reforming (APR). This method is used to convert many material that has carbon to a syngas. Then, syngas can undergoes reaction process such as Fisher-Tropsch synthesis to produce alkanes, methane via methanation and methanol by methanol synthesis. One of the uses of this syngas is as a fuel to manufacture steam or electricity. Another use is as a basic chemical building block for many users in the petrochemical and refining industries.

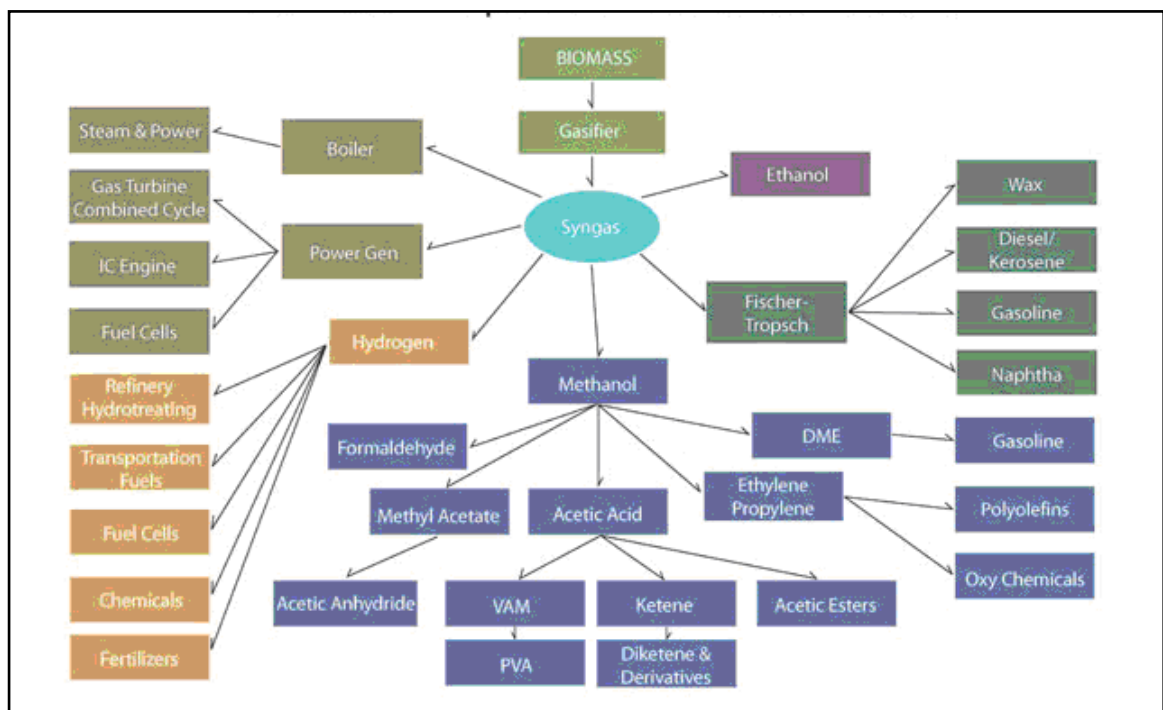


Figure 2.2 : The multitude of bio-based products that can be produced from syngas

2.3 Hydrogen gas

Hydrogen is a naturally occurring gas that is amazingly light. In fact, hydrogen is the lightest gas ever found. Hydrogen has no color, no smell and no taste. The hydrogen atom is so simple and small, it is hard to believe that hydrogen is the most important and abundant substance in the universe. Hydrogen atoms are the building blocks of other atoms.

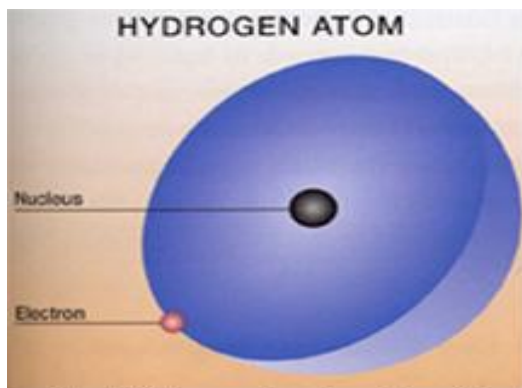


Fig. 3: Computer drawing of a hydrogen atom

The hydrogen atom has only one electron circling the nucleus. Hydrogen is the simplest element as it has only one nucleus in the middle of the atom, one shell which consists of one electron.

Pure hydrogen gas is very hard to come by, as it exists only in small underground pockets. This means that hydrogen may need to be produced artificially, from either fossil fuels or water. The splitting of hydrogen compounds uses a lot of energy. Currently most hydrogen is made by passing steam through natural gas, creating a compound of carbon monoxide and hydrogen. The compound is purified by changing the carbon monoxide to carbon dioxide and then the carbon dioxide is dissolved in water. Hydrogen is left behind after this process.

Scientists are looking for new methods of producing hydrogen that are more environmentally friendly. So APR is one of the methods that can be used in producing hydrogen. Hydrogen can be used for many things from a simple role like a lifting agent for a balloon until to most complex application such as a fuel for rockets and car.

In chemical processes, hydrogen can be an essential part in many chemical processes. Some of the chemical process which requires hydrogen is in production of acid such as hydrochloric acid. Hydrogen gas is also plays a big role in the processing of petroleum products to break down crude oil into fuel oil, gasoline and such. Besides, hydrogen is also important in producing ammonia NH_3 for used in making fertilizer.

Therefore, it is very important to find an alternative way to regenerate hydrogen from the biomass source because hydrogen can be used in many applications. As hydrogen is a very flammable gas, so it is very suitable to be used as a fuel for vehicle.

2.4 Processes To Produce Hydrogen or Syn Gas From Glycerol

2.4.1 Pyrolysis

Pyrolysis process produce two products which are in liquid and gaseous form. The liquid will be obtained at a temperature of 400 °C to 600 °C meanwhile for gas it happens at a high temperature which is >750 °C. The pyrolysis can be carried out in two different way which are with a presence of carrier gas or without any carrier gas. Chaudhari and Bakhshi (2002) carried out the pyrolysis of glycerol at 400 °C and 500 °C with glycerol flowrate at 2.0 g/h. As a result they found that a formation of char at the inlet of feed and it was not easy to carry out the experiment without a carrier gas.

In the case of using nitrogen as a carrier gas with the flowrate of 50ml/min in a packed bed reactor, glycerol can be fully converted to gas at the temperature of 700 °C with no liquid product was obtained. The gaseous product consist of syngas (hydrogen and carbon monoxide) which rich with hydrogen.

2.4.2 Steam Gasification

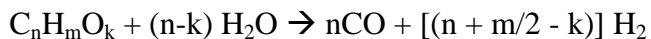
Basically gasification process is similar to pyrolysis but the major different between the two process is gasification is conducted in a presence of oxygen in a form of pure oxygen, steam or air. Chaudhari and Bakhshi (2002) reported that when glycerol

undergo a steam gasification process with steam flow rate of 2.5g/h, 5g/h and 10g/h and glycerol is flow at the rate of 4g/h. From the result obtained, it shown that about 80wt% of glycerol was converted when steam flow at rate of 10 g/h at 700 °C. It produced more than 90mol% of syngas with approximately H₂/CO ratio of 2. From the previous study, syn gas can be converted to to hydrogen via water-gas shift reaction and can be used as a green fuel for fuel cell. A part from that, syn gas can also be converted to green diesel by using Fisher-Tropsch reaction.

Stein and Antal (1983) reported that about 76.4 mol% of syngas was produced when glycerol go through a steam gasification process in a laminar flow reactor in gas phase, homogenous reaction. Syn gas produced consist of only 32.9 mol% of hydrogen and 43.5 mol% of carbon monoxide. This happened at a temperature of 700 °C with a major liquid products of acrolein and acetaldehyde and a yields of 52 mol% and 48 mol% respectively.

2.4.3 Catalytic Steam Reforming

Catalytic steam reforming of organic compounds is one of the process used to produce hydrogen. Catalyst used will not effect the component in the reaction but it is used to increase the reaction rate by decreasing the activation energy and to increase the yield of hydrogen. Steam reforming reactions of any oxygenated organic compounds such as glycerol and acetaldehyde proceeds according to the following equation (Czernik, 2002) ;



Because of the excess steam used in the process, carbon monoxide undergoes further reaction which is water-gas shift reaction to produce hydrogen and carbon dioxide. Research has been also carried out to produce hydrogen from biomass-derived oxygenated compounds such as methanol, glycerol and ethylene glycol using catalytic aqueous phase reforming reaction (Davda, 2003).

Czernik et. Al (2003) carried out catalytic steam refoming of bio oil derived fractions and crude glycerine using fluidized bed reactor to produce hydrogen. The lifetime of catalyst in fluidized bed reactor can be longer as compare to fixed bed or other reactor. During the experiments, 150g – 200g of a commercial nickel based catalyst was used. Catalyst was fluidized by the superheated steam. They reported that crude glycerol was a very viscous liquid and partially miscible with water. The temperature of crude glycerol was maintained at 60 – 80 °C because of its high viscosity. They suggested that a lower viscosity, it was easier to pump and atomize. The glycerol was fed at rate of 70 g/h, GHSV = 1600/h and steam rate at 145 g/h. Therefore, the steam/carbon ratio was 2.3.

Concentration of major gaseous product was found to be constant but, there was an increase in methane production from 500 ppm to 2200 ppm when the run time increased from 0 to 250 minutes. The hydrogen yields were around 77 wt%. If the amount of steam used is higher it may lead to the increase hydrogen yield. Via water-gas shift to produce carbon dioxide and hydrogen, this will enhance the yield to about 95 wt%. These results showed that a commercial value of a by-product from biodiesel production could become a viable renewable material for producing hydrogen. They suggested that integration of water-gas shift reaction and fluidized bed technologies would enhance the production of hydrogen and make it economically feasible.

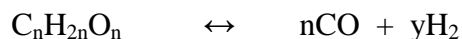
2.4.4 Aqueous Phase Reforming

Aqueous phase reforming (APR) produces syngas which contains with hydrogen and carbon monoxide. From biomass-derived oxygenated compounds such as sugar, sugar alcohol and glycerol. Using other biomass components such as starch and cellulose requires that they first be converted into water-soluble compounds before it can be use as a raw material to produce syngas via aqueous phase reforming.

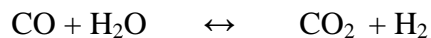
APR is unique in that the reforming is done in the liquid phase. It occurs at a relatively low temperature (200 °C – 250 °C) and pressure. Because of this reasons it is possible to generate hydrogen with low level of carbon monoxide in a single high

pressure chemical reactor. In addition, the water-gas shift reaction is favorable to be happened at this temperature and pressure condition. However, formation of alkane is highly favorable (C_nH_{2n+2}) in this low temperature condition from the reaction of H_2 with CO_2 or CO . APR is conducted at pressure (typically 15 – 50 bar) where hydrogen-rich effluent can be effectively purified using pressure- swing adsorption or membrane technologies. The chemical reactions involve in APR are;

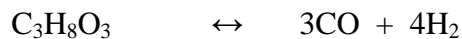
Low temperature reforming



Water-gas shift



As the raw material for this research is glycerol, the chemical reactions taking place in APR are;



Carbon monoxide can further react with water to form carbon dioxide. The reaction is as below;



Thus, the overall reaction of the glycerol in APR is



Therefore, from the reaction above it shows that when 1 mol of glycerol reacts with 3 mol of water it will gives 7 mol of hydrogen and 3 mol of carbon dioxide as a product.

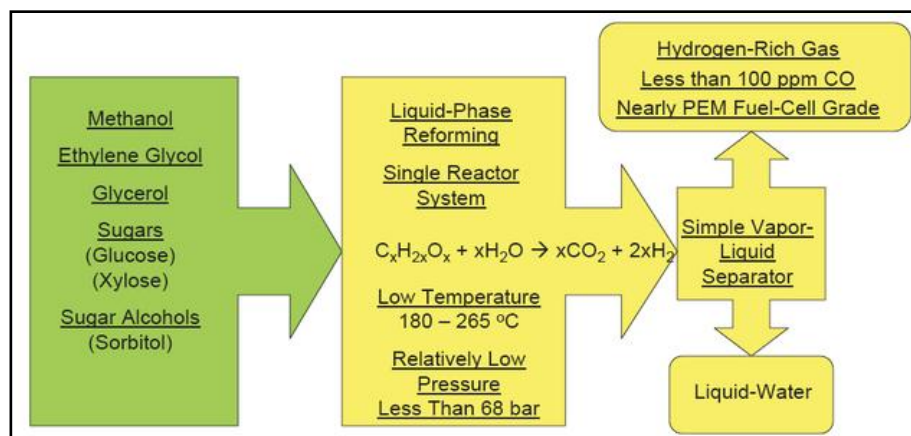


Figure 2.3 : The APR process

However, during the APR process taking place at a low temperature hydrogen gas and carbon dioxide which are produced are very unstable in a thermodynamic point of view because of the formation of alkanes such as methane and ethane. Hence, it is better to have a kinetic control of reaction pathway during the APR process. There are two main reaction pathway which are C-C bond and C-O bond cleavage pathway. It is good to have a C-C bond cleavage activity as it favors production of hydrogen to occur during the process. On the other hand, if C-O bond cleavage occur, there will be more alkanes produced during the reaction time.

In a Figure 2.4, it shows that the reaction pathway involved in the formation of H_2 and alkanes from oxygenated hydrocarbons over metal catalyst. Initially, dehydrogenation of reactant occurred on the metal surface to give absorbed intermediates. After that only C-C bond and C-O bond cleavage can happened. With platinum, the activation energy barriers is lowered for cleavage of O-H and C-H bonds. However, Pt-C bonds are more stable than Pt-O bonds, thus absorbed species are probably bonded preferentially to the catalyst surface through Pt-C bonds (Cortright). Cleavage bond of C-C leads to a formation of CO and H_2 and CO will undergo water-gas shift reaction to produce more hydrogen and carbon monoxide.

Hydrogen from Biomass-derived Hydrocarbons

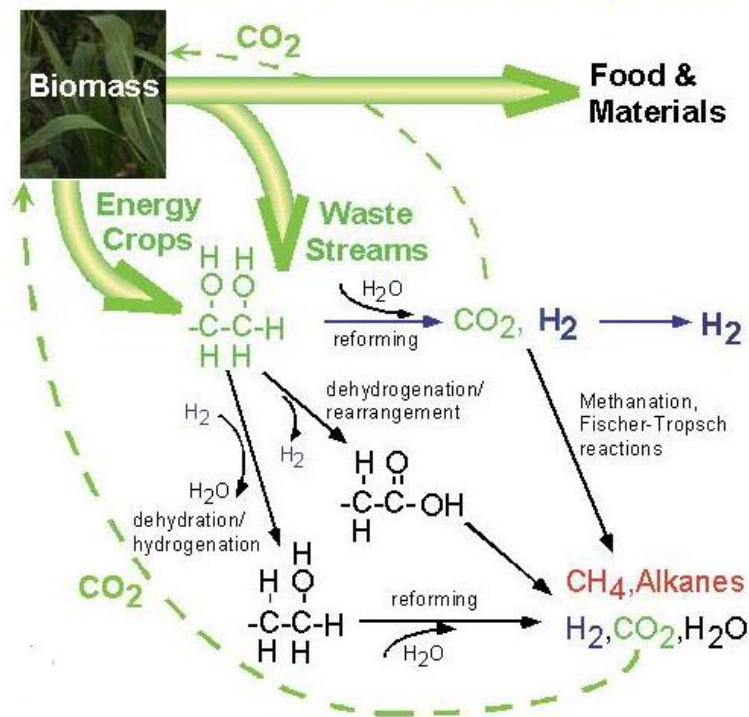


Figure 2.4 : Reaction pathway for reaction of oxygenated hydrocarbons with water to produce hydrogen

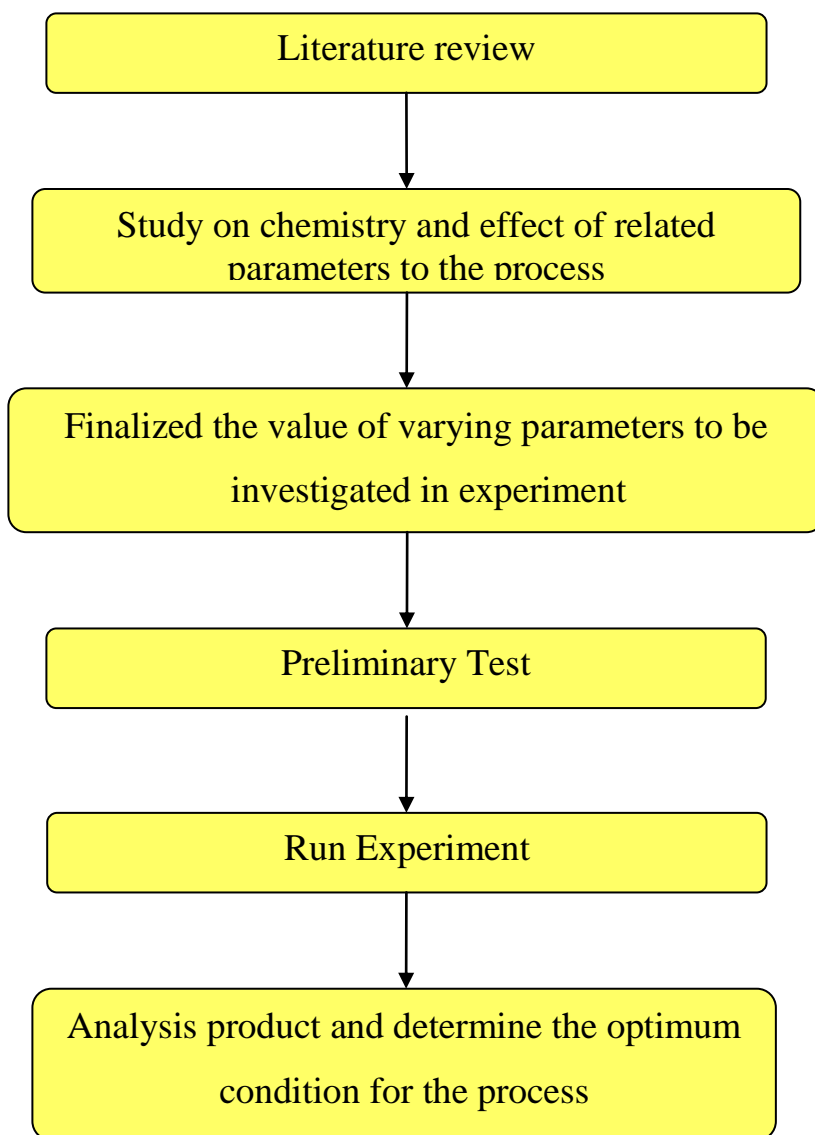
Since Group VIII metals possess higher activity for C-C bond cleavage and Pt and Pd catalyst displayed higher reforming activity than other metals. In addition, reaction kinetic studies for APR of ethylene glycol over various supported metals show that give higher selectivity towards hydrogen. Other metals such as Ni and Ru provide good catalytic activity but it cannot avoid formation of alkanes during the reaction and metals such as Rh, Ir Co, Cu, Ag, Au and Fe have low reforming activity for APR reaction. Instead of using Pt, a non precious metals such as Ni, Sn and Al are also can be used for the APR. However, these metals will be modified to increase their selectivity towards hydrogen and lower down the selectivity of alkanes formation during the reforming process.

Good catalyst should be selected and used in APR in order to increase the yields of hydrogen. Catalyst can help in reducing the formation of alkanes and organic acid. Catalyst should facilitate C-C bond cleavage and promote removal of adsorbed carbon monoxide by Water Gas Shift (WGS). In a same time, catalyst must not facilitate C-O bond cleavage and hydrogenation of CO or CO₂. Raney-NiSn and Pt/Al₃O₂ catalyst give an equal result toward reaction which can decrease the rate of methane formation and gives no effect to the production rate of hydrogen.

CHAPTER 3

METHODOLOGY

3.1 Flow of the research work



3.2 Equipments

There are only two equipments used in this experiment. The equipments are;

1. High pressure PARR batch reactor
2. Gas Chromatography (GC)

3.2.1 High pressure PARR batch reactor

Lab scale high-pressure PARR batch reactor will be use in this experiment. This reactor is available in UTP Laboratory in block 3. The reactor can be operated in high temperature and high pressure application. The volume of the reactor is 1000ml



Figure 3.1: Lab scale high pressure PARR batch reactor

3.2.2 Gas chromatography

An effluent gas produced from the aqueous phase reforming reaction will be collected by using a gas bag. The gas will then be transfer to Gas chromatography (GC) in order to analyze the composition of the effluent gas. The gas will be transported through the column by a carrier gas which is chemically inert. Commonly used carrier gases are helium and nitrogen. The carrier gas system also contains a molecular sieve trap to remove water and other impurities The GS itself was equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). FID is used to detect common hydrocarbon gases such as alkanes, ethylene and acetylene. Meanwhile, TCD is used to detect the amount of hydrogen, oxygen carbon monoxide, carbon dioxide and nitrogen. TCD will be used for this project as the main concerns only towards hydrogen gas produced from the APR process. Agilent G-1540A Gas Chromatography was used for this project to analyze gas products.

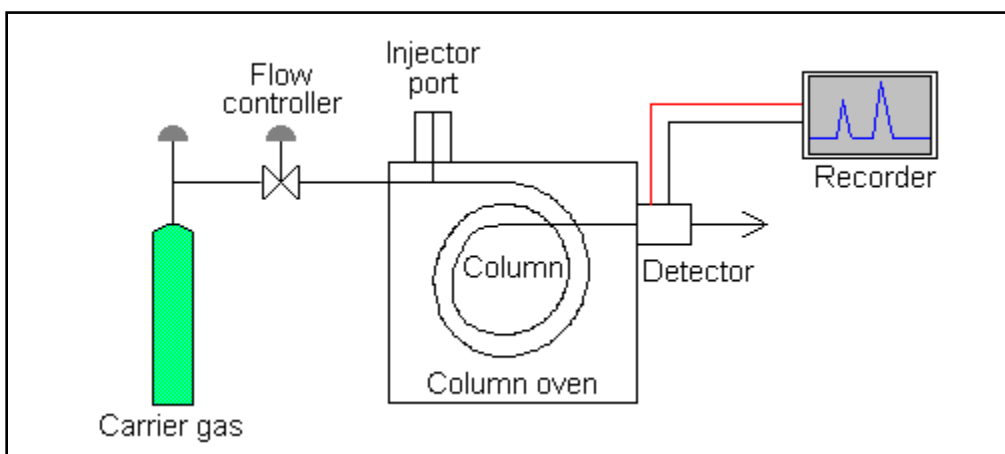


Figure 3.2 : Schematic diagram of Gas Chromatography

3.3 Experiment Details

The purpose of the experiment is to investigate the optimum state for the effects of temperature and catalyst to glycerol ratio with a constant value of inlet feed of glycerol, pressure and reaction duration for the process. The process variable for each process condition has been decided in order to meet the objectives of the research. For the experimental purposes, pure glycerol will be used throughout the project.

3.3.1 Inlet Concentration of glycerol

In order to achieve the objective of the research, which is determining the optimum process conditions in APR, an inlet concentration of glycerol should be constant throughout the experiment. Therefore, the inlet concentration of glycerol is set to be fixed at 10 wt%.

3.3.2 Catalyst

A catalyst was helped to speed up a chemical reaction since the process is conducted at a relative low temperature which favors alkanes such as methane. To overcome this, a good catalyst should be use in decreasing the rate of alkanes formation and increasing the selectivity of hydrogen production.

From the research done by Huber et al, 2004, it was recommended to use Raney-nickel stannum (ratio of 14:1) as a catalyst for APR because it can produce large amount of hydrogen and methanol as a liquid product. But due to a difficulty to find Raney-NiSn catalyst, so Pt/Al₂O₃ is decided to be used for this project as it was available at UTP. Consequently, further investigation of using Pt/Al₃O₂ as a catalyst will be done in this project. The three different concentration of Pt/Al₃O₂ will be used in this experiment. The amount of catalyst has been set to be 1.0 wt%, 2.0 wt% and 3.0 wt%.

Table 3.1 : Amount of catalyst used for APR Process

Catalyst Concentration (wt%)	Actual Mass of Catalyst (g)
1.0	1.461
2.0	2.922
3.0	4.383

3.3.3 Temperature

Temperature is the most important process condition that should be taken into consideration in determining the amount of hydrogen produced from glycerol in a aqueous phase. Pagliaro et al (2007) said that the suitable temperature for APR is between 200 °C to 250 °C using metal catalysts in a reactor. Two temperatures were selected for this experiment which are 210 °C and 230 °C.

3.3.4 Reaction duration

As for achieving the set temperature, the APR process was maintained and held at this temperature for at least 30 minutes in order to ensure all reaction was complete.

3.3.5 Pressure

The initial pressure of the APR reactor was fixed for all the experiments in order to compare the result obtained by varying temperature, concentration of catalyst and reaction duration. APR process starts when external pressure is injected into the reactor. For this experiment, compressed air is used to pressurize the reactor until the pressure inside the reactor is 50 psi or equivalent to 3.447 bar. Heat is supply simultaneously after the pressure inside the reactor achieved 50 psi. All of these process variables which will be investigated are as per table below.

Table 3.2 : Overall process variables to be investigated

Glycerol wt%	Catalyst wt%	Temperature (°C)	Duration (mins)
10	1.0	210	30
10	1.0	230	30
10	2.0	210	30
10	2.0	230	30
10	3.0	210	30
10	3.0	230	30

3.4 Experiment Setup and Procedure

Experiment was conducted by using lab-scale high pressure batch reactor which was available in UTP reaction engineering lab in Block 3.

i) Preparing the reactant

All the reactants which are glycerol, water and catalyst are weighted separately according to the calculation done before. This is a very important to ensure reaction between the glycerol and water was done in a complete reaction process based on the theoretical done.



Figure 3.3 : Weight the reactant

ii) Mixing of reactant

All the reactants are mixed together into a beaker. To ensure a perfect and uniform mixture, stirrer rod is used for this purpose. This should be done because the glycerol used for this experiment is a very viscous liquid and partially miscible with water. As all the reactants are well mixed, this will ensure that the mixture can be easily reacted chemically with the catalyst.



Figure 3.4 : Mixing the reactant

iii) *Insert reactant to reactor*

The measured catalyst was mixed together with the blended reactant and pour into the reactor system.

iv) *Setup the reactor*

The reactor system was tested for leakage. All the connecting valves were monitored cautiously because any leakage will result unachieved pressure reading. The APR process was started with the application of an external pressure into the reactor which is compressed air. When the set temperature is achieved, the process was maintained and held at least for 30 minutes in order to ensure all reaction were complete.

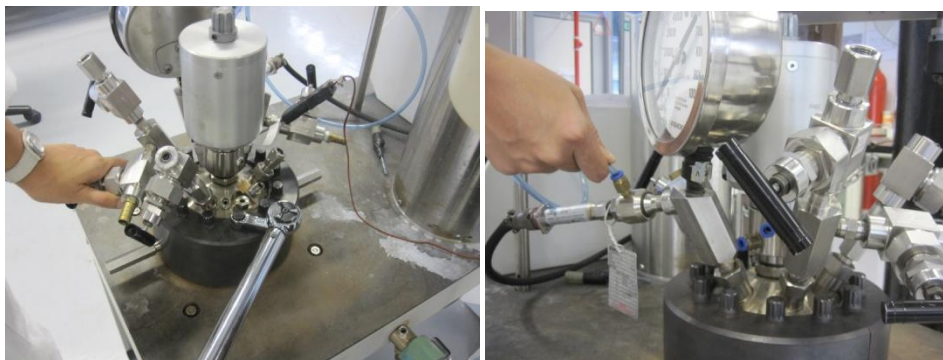


Figure 3.5 : Setup the reactor to make ensure no leakage

v) *End of Experiment*

The gas and liquid mixture were allowed to remain sat can cool down for at least 1 hour to decrease the pressure and temperature inside the reactor. The settling time was important to ensure that the hot product in the reactor did not sprout out all of the sudden due to high pressure inside the reactor. During the settling time, the slurry of glycerol, catalyst and the incomplete water vapor would settle down at the bottom part of reactor. The required gas product would float on the top and flowing out as the corresponding valve was opened.

vi) *Collect the gas products*

The gas product was collected by using a 0.5L Tedlar gas bag and ready to be sent for gas analysis.



Figure 3.6 : Collect gas sample by using gas bag

vii) *Gas Analysis*

Gas chromatography (GC) was used to analyze the composition of the gas product collected from APR process.



Figure 3.7 : GC test for the gas sample

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimental Results and Discussion

Experiment results shows that hydrogen is produced in aqueous phase reforming process. As stated in theory, every mole of glycerol must be contains with four moles of hydrogen.

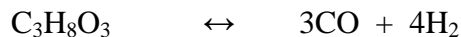
In standard composition of dry air, the gas consists of only 0.5 ppm hydrogen gas as shown in Table 4.1.

Table 4.1 : Standard Composition of dry air

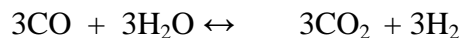
Gas	Chemical Symbol	% by Volume	% by Weight	ppm (by volume)
Nitrogen	N ₂	78.08	75.47	780805
Oxygen	O ₂	20.95	23.2	209450
Argon	Ar	0.93	1.28	9340
Carbon Dioxide	CO ₂	0.038	0.059	380
Neon	Ne	0.0018	0.0012	18.21
Helium	He	0.0005	0.00007	5.24
Krypton	Kr	0.0001	0.0003	1.14
Hydrogen	H ₂	0.00005	Negligible	0.5
Xenon	Xe	8.7 x 10 ⁻⁶	0.00004	0.087

APR involves two reactions in producing hydrogen which are shown as below:

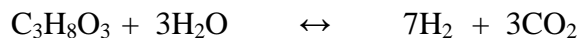
Low temperature reforming



Water-gas shift



So as an overall chemical reaction, there are seven moles of hydrogen produced in APR method.



Hydrogen gas is detected by the TCD at retention time of 4.165 min. In standard dry air, the gas consist of only small portion of hydrogen as stated in Table 4.1. The experiments had proven that the hydrogen gas has been produced because there are larger amount of hydrogen detected by using TCD. Table 4.2 shows a composition of gas product of APR experiment at various parameters.

Table 4.2 : Composition of gas product of APR experiment at various parameters

Feed		Temperature °C	Duration mins	Composition of products gas (mol %)			
Glycerol wt%	Catalyst wt%			CO ₂	H ₂	CO	Unknown
10	1	210	30	0.41705	34.2098	-	65.37315
10	1	230	30	2.15599	43.40292	-	54.44109
10	2	210	30	0.3279	49.1329	-	50.5392
10	2	230	30	8.32775	54.8655	2.4864	34.32035
10	3	210	30	4.9874	61.3537	2.83737	30.8215
10	3	230	30	8.3504	79.0275	2.0977	10.524

The amount of glycerol used in the experiment is 10 wt%, which is equivalent to 0.159 mol. In theoretical calculation attached in Appendix A.1, 0.159 mol glycerol will produce 1.113 mol of hydrogen. The Table 4.3 below shows the amount of hydrogen produced and its conversion factor.

Table 4.3 : Amount of hydrogen produced and its conversion factor

Feed		Temperature (°C)	Duration (min)	Hydrogen yield (mol)		Conversion (%)
Glycerol (wt%)	Catalyst (wt%)			Theoretical	Experimental	
10	1	210	30	1.113	0.3463	31.11
10	1	230	30	1.113	0.4340	38.99
10	2	210	30	1.113	0.4913	44.14
10	2	230	30	1.113	0.5486	49.29
10	3	210	30	1.113	0.6135	55.12
10	3	230	30	1.113	0.7903	71.0

From the results, it is observed that the highest yield of hydrogen gas which is 0.7903 mol has exhibit a conversion factor of 71.0%. This clearly states that there are still 29% amount of hydrogen content in glycerol is not converted into hydrogen gas. Instead, the hydrogen might have been converted into other form of hydrocarbon such as CH₄ and other compounds.

From the previous experiment, the hydrogen gas cannot be detected by GC. This is because all the samples were kept for a long time due to unavailability of Gas Chromatography. All the hydrogen gas can easily escape from the gas bag because the molecule of hydrogen is very small and light. In order to get avoid hydrogen escape from a gas bag, the experiment must be run again to get a fresh sample which can be tested immediately by using a GC.

No systematic studies have been carried out on the effects of the process parameters. Therefore, there is no standard comparison with other work in terms of hydrogen yield. Kamili (2006) reported that a 15% of hydrogen is produced by APR of glycerol with copperchromite catalyst at 225 °C. However the amount of catalyst used is not reported. Valliyappan (2004) reported that a hydrogen yield of 48.6 % at 800°C with quartz chip diameter of 3 – 4 mm. The steam gasification produced 32.9 mol % of hydrogen at 650 °C. The inconsistency of units, process parameters and production method restrained the comparison of which method is better in terms of conversion factor and its efficiency. But, since APR is operated at low temperature and low pressure as compare to other methods, it is believe that the mass production of hydrogen by using APR process is attainable.

4.2 Effect of Catalyst Concentration

The effect of catalyst concentration on hydrogen yield of glycerol is shown in Figure 4.1 and Figure 4.2. It is observed from the figures that hydrogen yield shows a linearly increased by increasing a catalyst concentration. For 210°C, hydrogen yield increase from 34.21% to 49.13% and up to 61.35% by using different catalyst concentration which are 1wt%, 2wt% and 3wt%. This trend is same goes for 230°C where hydrogen yield is increased by increasing the catalyst concentration. Both of temperature show that maximum yield occurs at catalyst concentration 3 wt%.

From theory, catalyst is used to increase the rate of reaction. So it can say that from result obtained, as the concentration of catalyst is increased the amount of hydrogen yield also increased. It is important to determine the optimum amount of catalyst to be used for the process. This is because it is possible that too much catalyst might cause the reaction to be over reacted and the produced hydrogen is dissociated to form other components. Hydrogen molecules can associate with oxygen to form water in a reverse reaction of APR.

For this project, the experiments of each condition are only run once. To improve the result and study the yield of gas more accurately, the experiment should be repeated for two or three times to get a better result and data analysis.

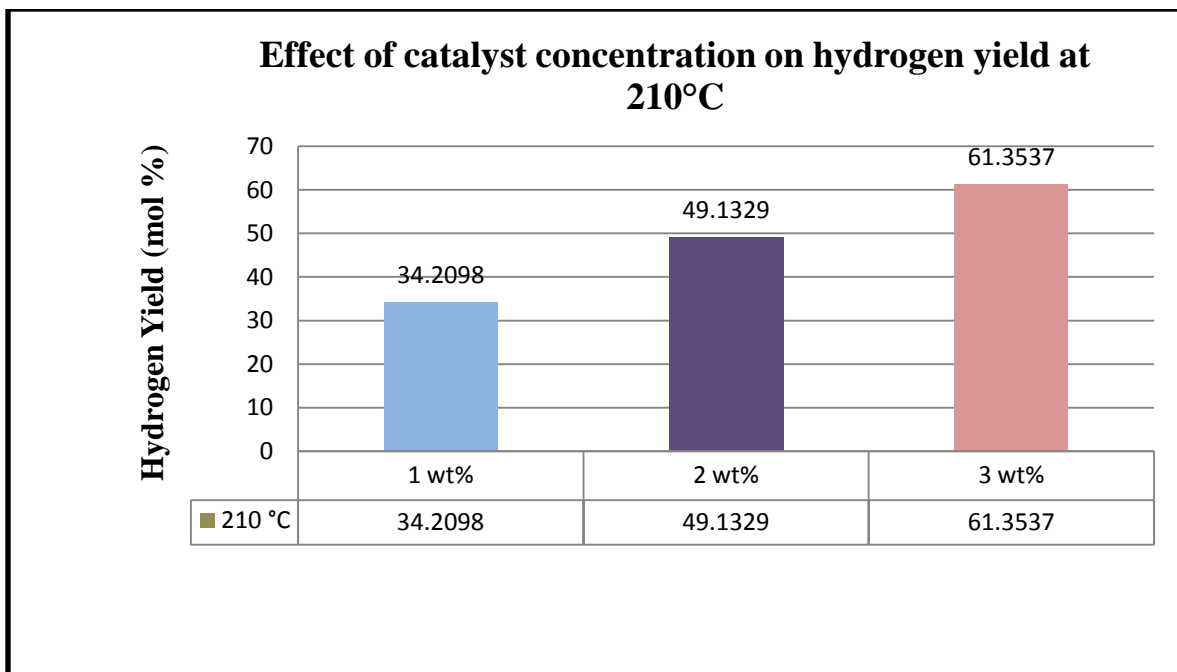


Figure 4.1: Effect of catalyst concentration on hydrogen yield at 210°C

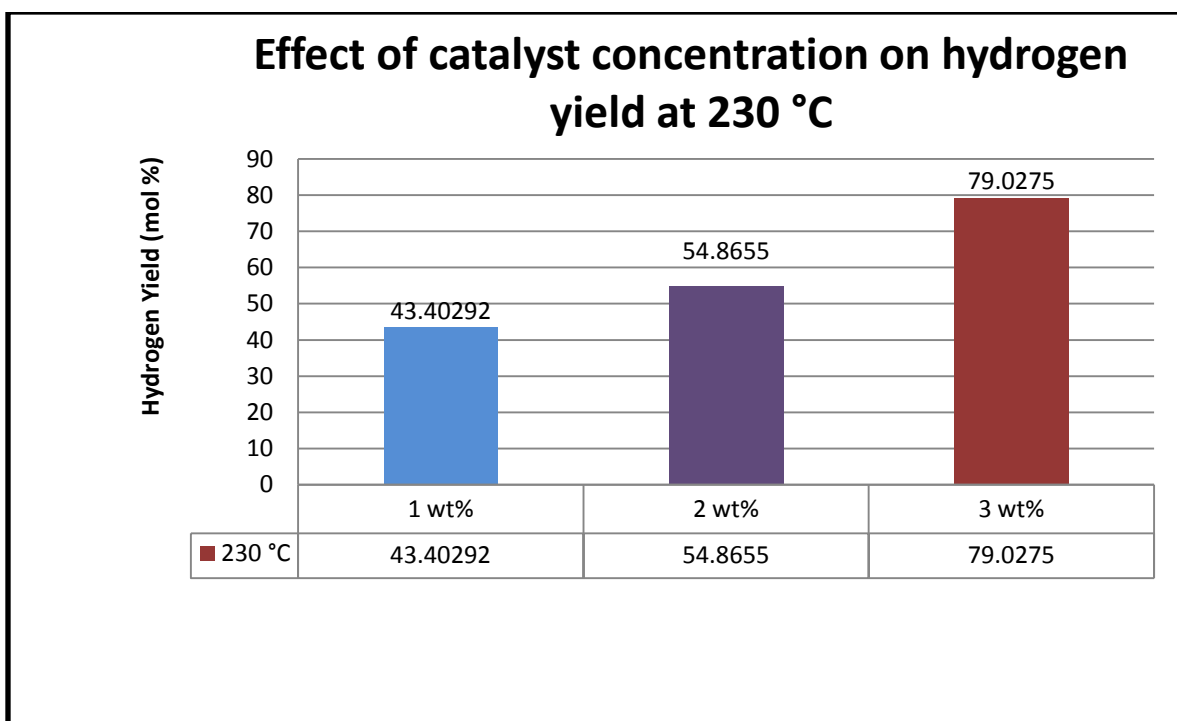


Figure 4.2 : Effect of catalyst concentration on hydrogen yield at 230°C

4.3 Effect of Temperature

In the increase of temperature of reaction has greatly affected the hydrogen yield. From the Figure 4.3, it is shows that by increasing the temperature from 210°C to 230°C hydrogen yield also increase for all catalyst concentration. For example for 2 wt% catalyst, hydrogen yield increase from 49.13% to 54.86% as the temperature increase from 210°C to 230°C. For 3 wt% of catalyst concentration, the hydrogen yield also shows a great increment value which is from 61.35% to 79.03% by increasing the temperature of the process.

From Table 4.2, it is observed that the amount of unknown compounds is decreased as the temperature is increased. Even though generation of hydrogen and carbon dioxide is favorable to be happened at this low temperature range but it is accompanied by selectivity challenges since the reaction of hydrogen with carbon dioxide or carbon monoxide to form alkanes is highly favorable at these low temperatures. The result shows that formation of alkanes can be reduce by increasing the temperature and catalyst concentration. In a nut shell, temperature plays an important role in APR process. It is a must to determine a suitable and an optimum temperature for APR process so that the formation of alkanes during the process can be suppressed. Thus, the production of hydrogen can me maximize.

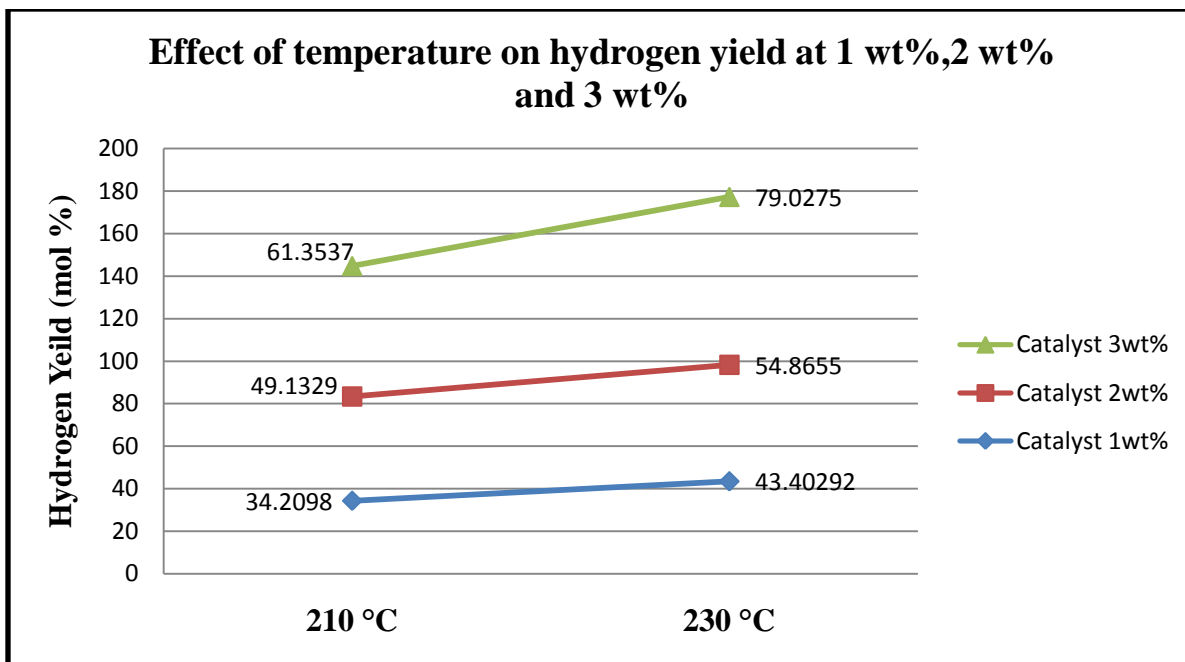


Figure 4.3 : Effect of temperature on hydrogen yield at various concentration of catalyst

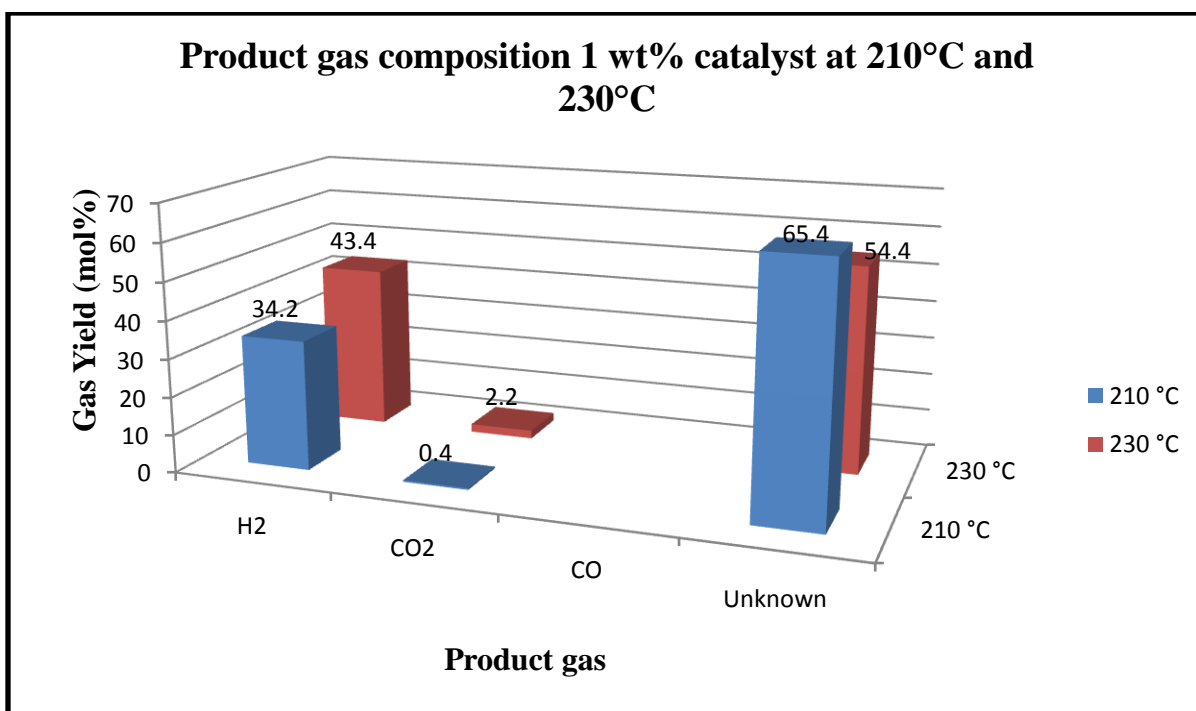


Figure 4.4 : Product gas composition by 1 wt% catalyst at 210 °C and 230 °C

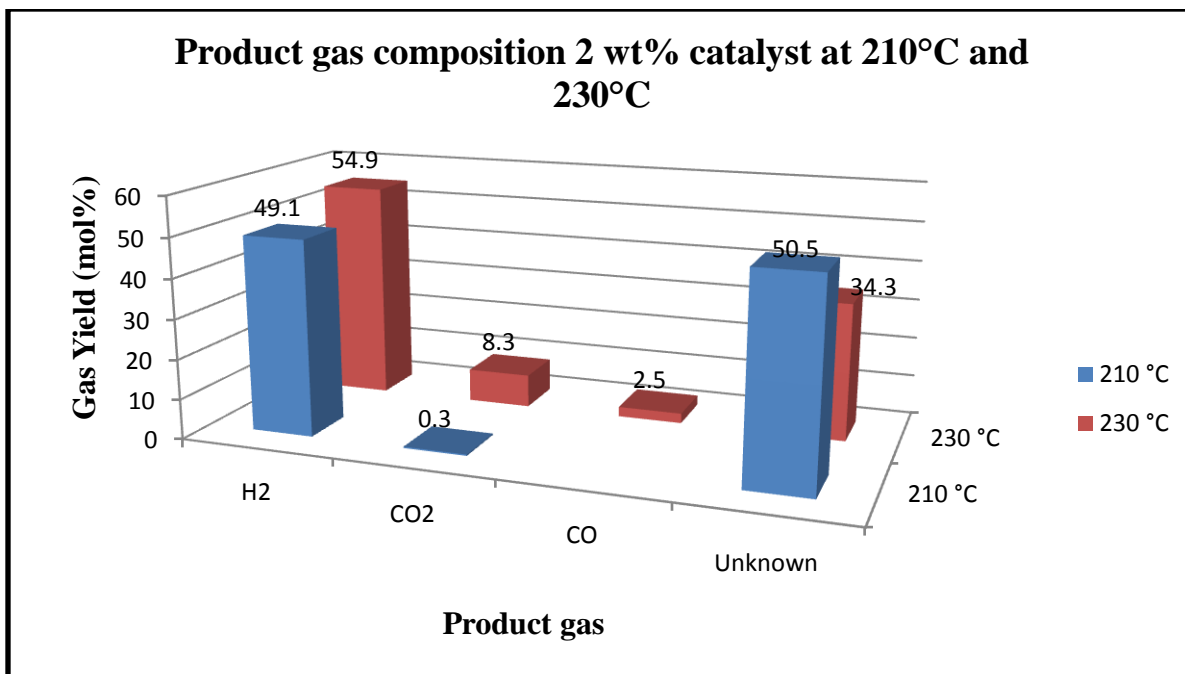


Figure 4.5 : Product gas composition by 2 wt% catalyst at 210 °C and 230 °C

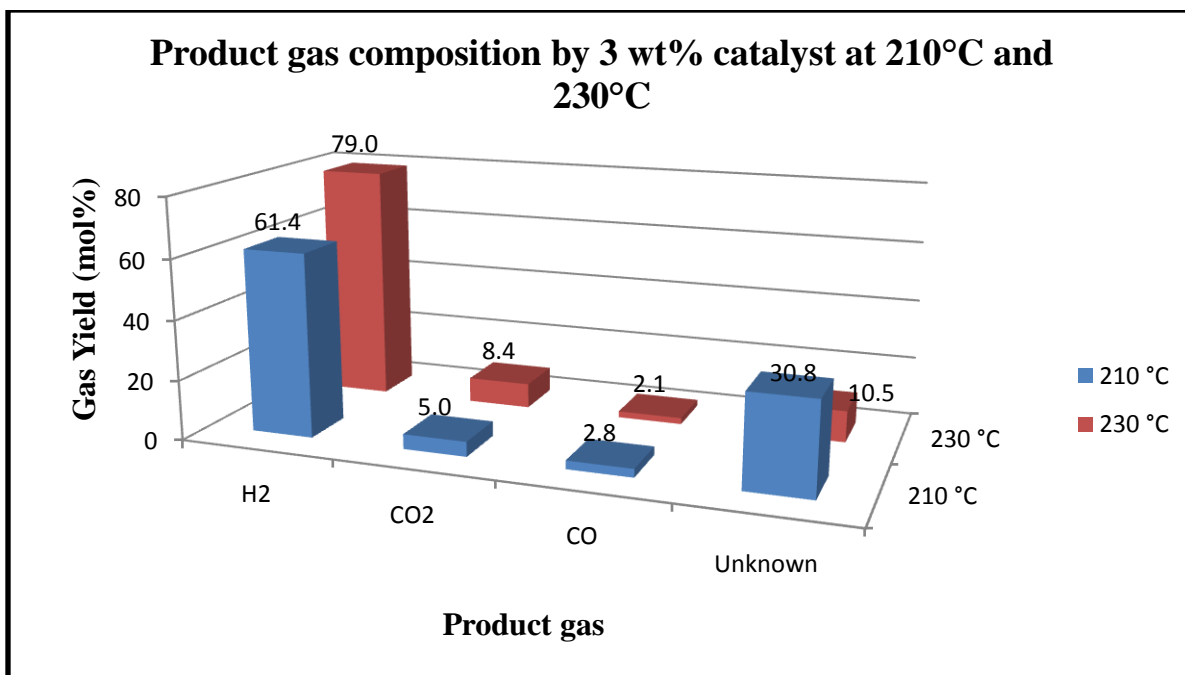


Figure 4.6 : Product gas composition by 3 wt% catalyst at 210 °C and 230 °C

4.4 Summary of results

From all the results obtained, it is found that that the optimum process condition for APR which produced the maximum yield of hydrogen is by using 3 wt% of catalyst concentration with a temperature of 230 °C. The amount of hydrogen produced under this process condition is 79.03 mol%. Figure 4.7 summarizes hydrogen yield at various process parameters. From the graph, it clearly state that by increasing the amount of catalyst will lead to maximizing the amount of hydrogen produced because catalyst will effects the reaction rate of the process. In addition, it is more effective to perform the reaction of glycerol at 230 °C instead of 210 °C because the result shows a constant increment of hydrogen yield as the temperature is increased.

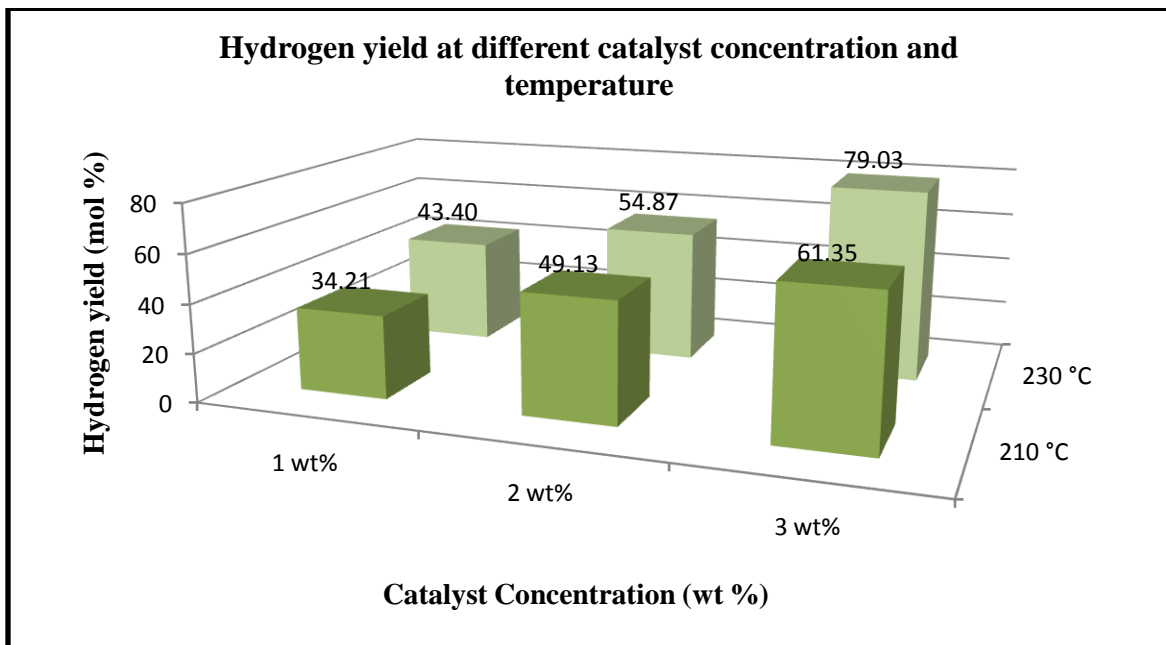


Figure 4.7 : Hydrogen yield at different catalyst concentration and temperature

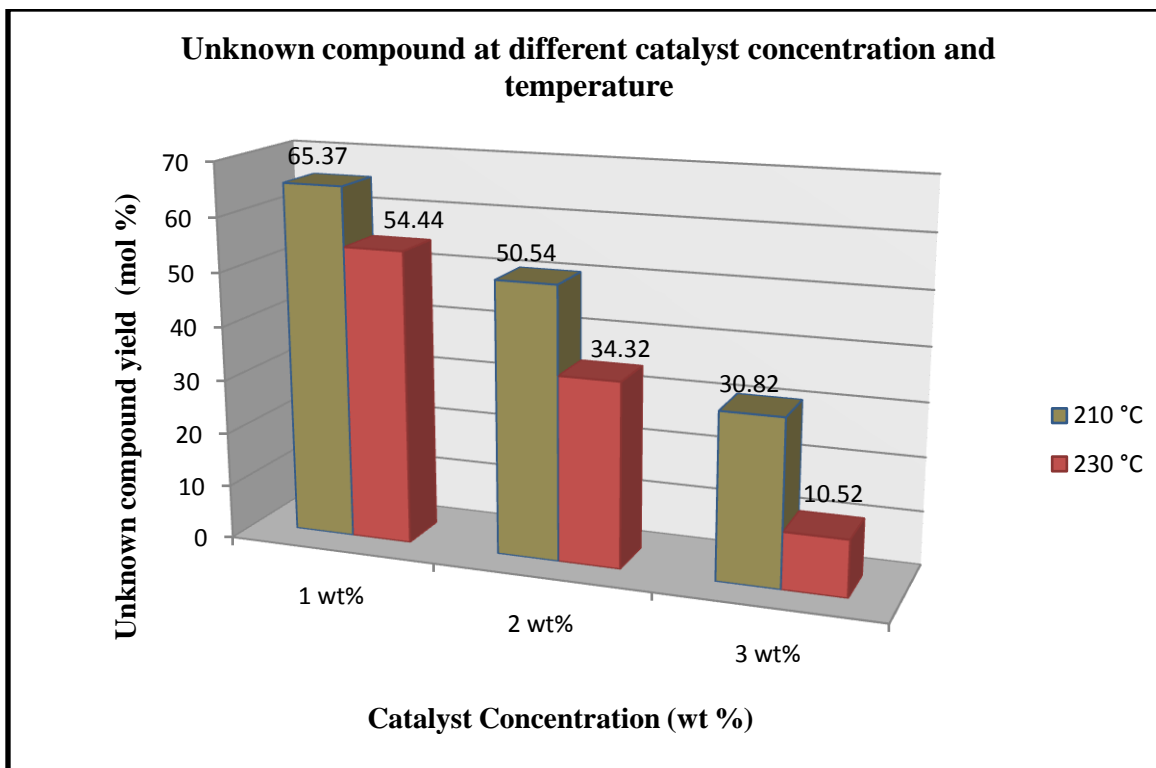


Figure 4.8 : Unknown compound yield at different catalyst concentration and temperature

From the results, other observation also can be made which is there are large amount of unknown compound in the gas products of APR as shown in Figure 4.8. The maximum amount of unknown gas can be as large as 65.37 mol% and the smallest value is 10.52 mol%. There are various types of components present in the unknown gas. The possible gas might be oxygen, nitrogen, hydrocarbons and others. NO_x also can be formed because of the process was done in high pressure condition. Also, water vapor also formed during the process. All these gases are undetectable by the GC. Due to a few circumstances the GC available in UTP lab can only detect carbon dioxide, carbon monoxide and hydrogen.

CONCLUSION

Based on the experiment which has been done for this research work, the results show that hydrogen can be produced and generated by using aqueous phase reforming of glycerol. APR can generate hydrogen at a lower temperature compare to other methods such gasification and pyrolysis processes.

The parameters investigated in this project are catalyst concentration and temperature of the reaction. The varying a concentration of catalyst, the results obtained showed that the hydrogen yield is dramatically increased as the concentration of catalyst increased. The hydrogen yield has increased up to 50% for 1 wt% to 3 wt% of catalyst. Reaction at higher temperature which is 230 °C can produce more hydrogen as compare to 210 °C. The maximum amount of hydrogen can be produced at 230 °C is 79.03 mol% and maximum hydrogen can be produced at 210 °C is only 61.35 mol%.

As a conclusion, an optimum process condition for aqueous phase reforming in order to maximize the generation of hydrogen gas is at a temperature of 230 °C together with 3 wt% of catalyst concentration.

From the previous study, it shows that hydrogen generation from glycerol has a great potential for further development.

RECOMMENDATIONS AND FURTHER WORK

Further development and research are needed to be done in order to commercialize the hydrogen generation from waste glycerol. There are many limitations in the work that could be improved.

All the samples from the previous experiment are stored inside the gas bag for a quit long time. Apparently the hydrogen molecule can be escaped from the gas bag. In order to get an accurate result, the fresh sample must be analyzed immediately by using the GC. All the experiments should be repeated at least thrice to get more constant results.

Before running any of the experiment, the reactor must be checked first to ensure it can operate at its optimum condition. All parts must be well function able especially the stirrer. The faulty of reactor system might effects the output of the process which is the desired gas products

It is highly suggested to analyze the liquid product of the APR process. From that, the amount of unconverted glycerol and other compounds can be detected. Both of the findings can be compared to make sure that the results obtained are accurate and precise.

Huber et al (2003) has reported that in order to get a higher yield of hydrogen, APR process should be carried out at higher temperature which is at 250 °C. This is because at this temperature it can decrease the rate of methane formation which later exhibit highest water-gas shift reaction.

To commercialize the hydrogen generation from waste glycerol, an effective cost feasibility study should be carried out to investigate the hydrogen production cost against it's saving and benefit.

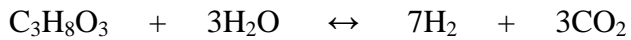
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APPENDIX

A.1 Theoretical Calculation



Molecular Weight :

Glycerol, $\text{C}_3\text{H}_8\text{O}_3 = 92.09 \text{ g/mol}$

Water, $\text{H}_2\text{O} = 18.015 \text{ g/mol}$

Total weight of reactant, m

$$\frac{92.09g}{\text{mol glycerol}} \times 1 \text{ mol glycerol} + \frac{18.015g}{\text{mol water}} \times 3\text{mol water}$$
$$= 146.135 \text{ g}$$

For 10 wt% of feed concentration

= feed concentration x mass of reactant

$$\frac{10}{100} \times 146.135g = 14.613 \text{ g}$$

Mass of water, m_w

= mass of reactant – mass of glycerol

$$= 146.135g - 14.61g$$

$$= 131.522g$$

Calculation for Catalyst Platinum alumina ($\text{Pt}/\text{Al}_3\text{O}_2$)

For 1.0 wt% catalyst concentration, m_c

$$\frac{1.0}{100} \times 146.135g = 1.461 \text{ g}$$

$$2.0 \text{ wt\%} = 2.922g$$

$$3.0 \text{ wt\%} = 4.383g$$

Total Mol of Glycerol (C₃H₈(OH)₃)

$$\begin{aligned}\text{Mol} &= \frac{\text{Mass}}{\text{Molecular Weight}} = \frac{14.613}{92.09} \\ &= 0.159 \text{ mol of glycerol}\end{aligned}$$

From equation,

1 mol of glycerol will produced 7 mol of H₂ gas.

$$0.159 \times 7 \text{ mol} = \mathbf{1.113 \text{ mol of H}_2}$$

Conversion

$$\begin{aligned}\text{Conversion} &= \frac{\text{Experimental value}}{\text{Theoretical Value}} \\ &= \frac{0.7903}{1.113} \times 100 \\ &= 71.0 \%\end{aligned}$$

A.2 Data Gathering

Example of Result Sheet

Sample name : Run 1 Exp 6

Date: 7 April 2010

Condition : 3.0 wt% Pt/Al₃O₂, 30 minutes reaction duration, 230 °C

Mass of Glycerol (g): 29.227g

Mass of water (g): 263.043g

Catalyst : Pt/ Al₃O₂

Mass of catalyst: 4.383g

Temperature : 230 °C

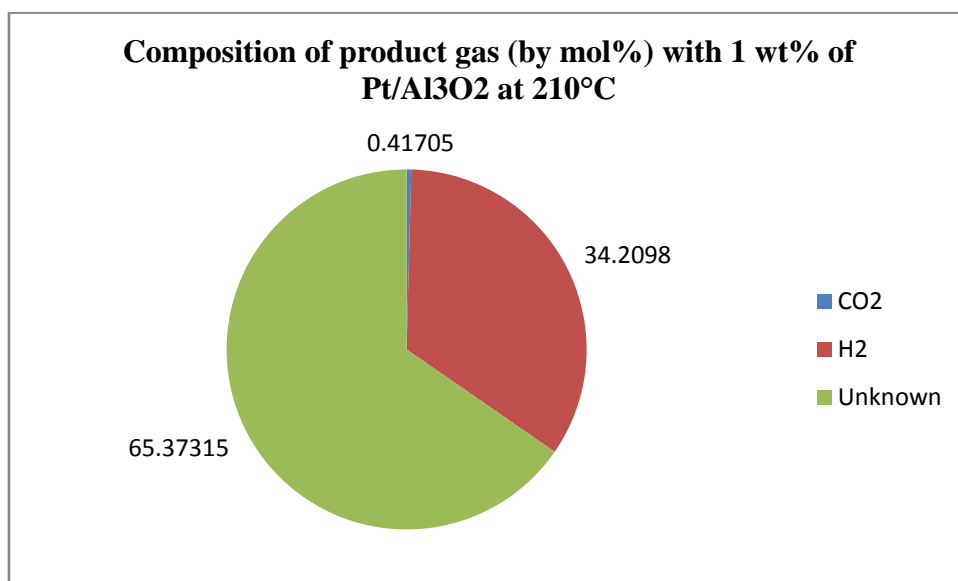
Pressure (bar): 50 Psi / 3.447 Bar

Time (Min)	Temperature (°C)	Pressure (Psi)	Remarks
0	25	50	
10	51	70	
20	80	80	
30	101	90	
40	127	100	
50	140	110	
60	158	130	
70	170	150	
80	181	200	
90	189	230	
100	195	260	
110	201	280	
120	210	290	
130	218	305	
140	225	310	
150	230	330	
160	230	330	
170	230	330	
180	230	330	

A.3 Data Analysis

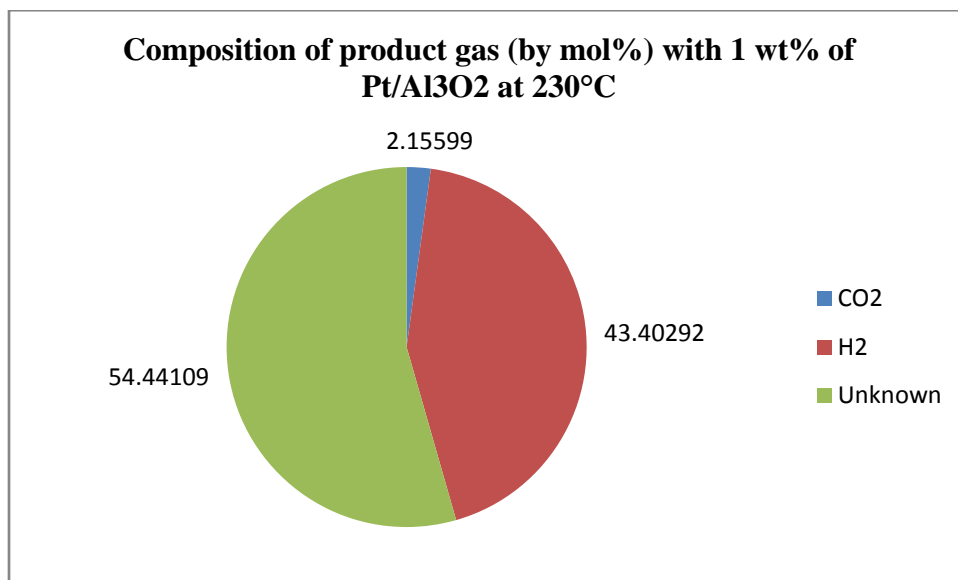
A.3.1 Experiment 1 (1 wt% catalyst concentration at 210°C)

<i>Catalyst = 1.0 wt% and 210°C</i>					
Gas	RT (min)	Area	Amt/area	Amount (mol %)	Mol
CO ₂	2.723	116.33	0.003585	0.41705	0.0041705
H ₂	4.165	178.1	0.192081	34.2098	0.342098
Unknown				65.37315	0.6537315
Total				100	1



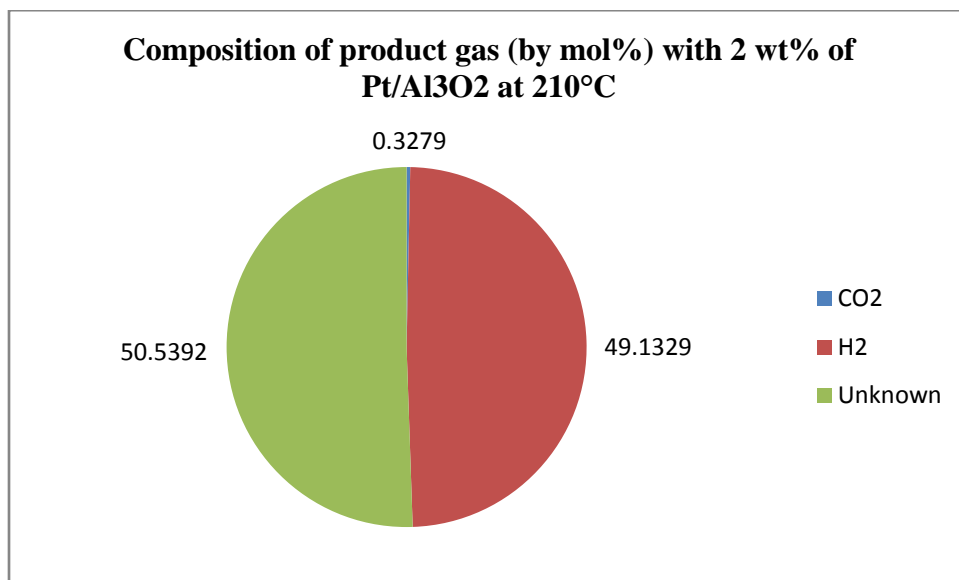
A.3.2 Experiment 2 (1 wt% catalyst concentration at 230°C)

<i>Catalyst = 1.0 wt% and 230°C</i>					
Gas	RT (min)	Area	Amt/area	Amount (mol %)	Mol
CO ₂	2.723	601.373	0.003585	2.15599	0.0215599
H ₂	4.165	225.9617	0.192081	43.40292	0.4340292
Unknown				54.44109	0.5444109
Total				100	1



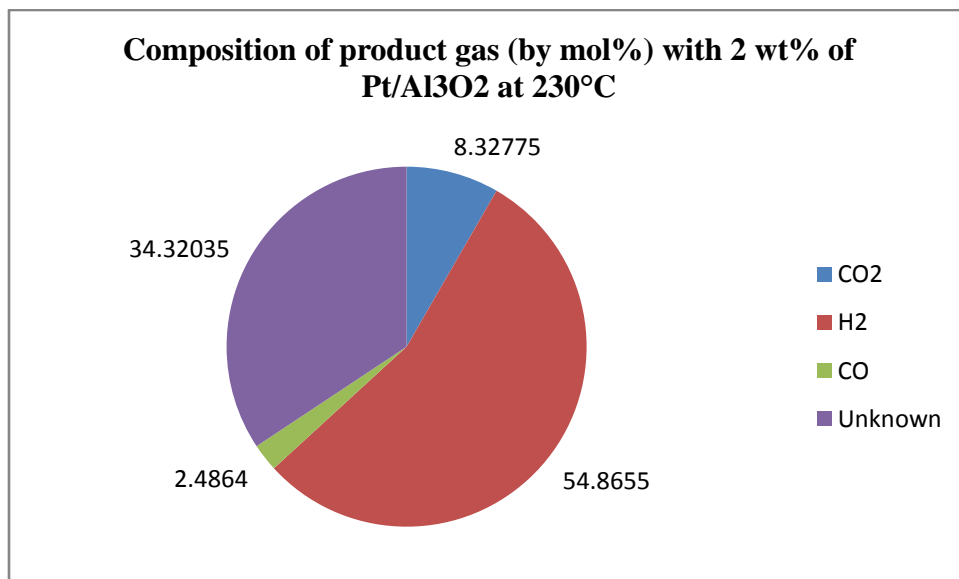
A.3.3 Experiment 3 (2 wt% catalyst concentration at 210°C)

<i>Catalyst = 2.0 wt% and 210°C</i>					
Gas	RT (min)	Area	Amt/area	Amount (mol %)	Mol
CO ₂	2.723	91.48	0.003585	0.3279	0.003279
H ₂	4.165	255.79	0.192081	49.1329	0.491329
Unknown				50.5392	0.505392
Total				100	1



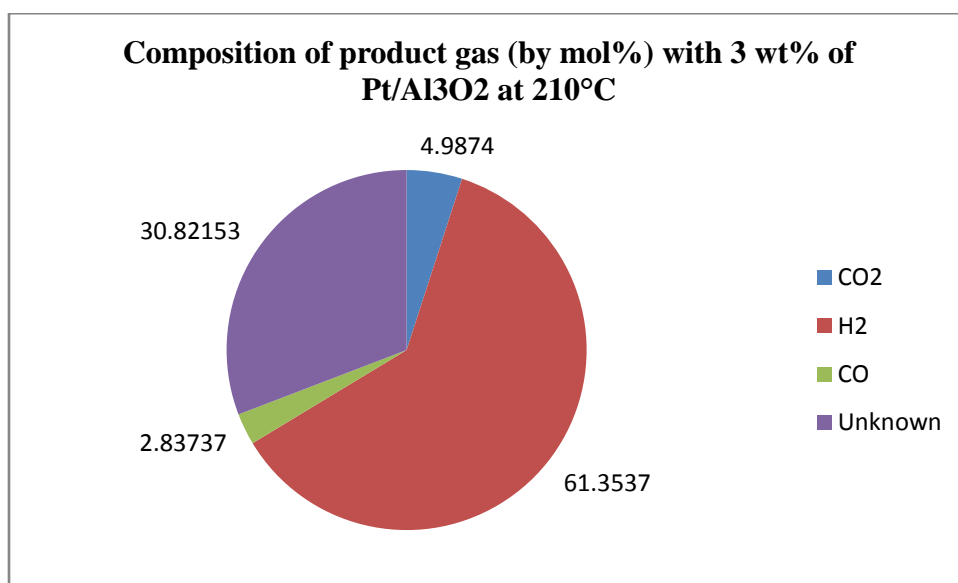
A.3.4 Experiment 4 (2 wt% catalyst concentration at 230°C)

<i>Catalyst = 2.0 wt% and 230°C</i>					
Gas	RT (min)	Area	Amt/area	Amount (mol %)	Mol
CO ₂	2.723	2322.86	0.003585	8.32775	0.0832775
H ₂	4.165	285.64	0.192081	54.8655	0.548655
CO	4.988	639.66	0.003887	2.4864	0.024864
Unknown				34.32035	0.3432035
Total				100	1



A.3.5 Experiment 5 (3 wt% catalyst concentration at 210°C)

<i>Catalyst = 3.0 wt% and 210°C</i>					
Gas	RT (min)	Area	Amt/area	Amount (mol %)	Mol
CO ₂	2.723	1391.129	0.003585	4.9874	0.049874
H ₂	4.165	319.416	0.192081	61.3537	0.613537
CO	4.988	729.92	0.003887	2.83737	0.0283737
Unknown				30.82153	0.3082153
Total				100	1



A.3.6 Experiment 6 (3 wt% catalyst concentration at 230°C)

<i>Catalyst = 3.0 wt% and 230°C</i>					
Gas	RT (min)	Area	Amt/area	Amount (mol %)	Mol
CO ₂	2.723	2329.18	0.003585	8.3504	0.0835
H ₂	4.165	411.43	0.192081	79.0275	0.7903
CO	4.988	539.63	0.003887	2.0977	0.021
Unknown				10.524	0.1052
Total				100	1

