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# Abstract

Aqueous-phase reforming (APR) is a relatively recent technology for producing hydrogen from biomass-derived substrates. Amidst the worldwide concerns about increasing petroleum prices and declining supplies, this process has the potential to address the need for a readily-available source of energy that is renewable and environment-friendly. APR uses temperatures much lower than those used in existing thermochemical methods for biomass: ~500K as opposed to about 600K to 1100K for pyrolysis and gasification. The reaction occurs in aqueous phase in the presence of a reforming metal catalyst that can catalyze both reforming and water-gas shift reactions. To date, known APR studies dealt only with applying this technology to oxygenated compounds that were used to mimic biomass. However, it is considered that application of APR to real biomass is needed to gauge whether this technology can be considered a viable approach for hydrogen production.

This study deals with the first known application of APR for the production of  $H_2$  from actual biomass. For this project glucose was used. The experiments were carried out in batch using a 100mL Parr High Pressure Reactor heated to 230°C. These simple compounds were then reformed using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The gas-phase products were typically  $H_2$ , CO<sub>2</sub> and CO. Gas Chromatograph (GC) with thermal conductivity detectors (TCD) were used in order to quantify the gas phase.

The objective of this research is to carry out a series of hydrogen generation experiments at varying conditions to study the effects of catalyst concentration, and temperature. Consequently, the optimum state for hydrogen production from glycerol can be determined and a processor is designed to produce the hydrogen at its maximum yield.



The amounts of catalyst concentration used are 1 wt%, 3 wt% and 5 wt%. Effect of increasing catalyst concentration from 1 wt% to 3 wt% for 90 minutes reaction duration had shown the hydrogen yield increase by 18.87% from 0.6745679 moles at 230 deg C then decreases to 5.20% to 0.7601504 moles at 5wt% of catalyst. Similar trend is also observed for 90 minutes duration where the maximum point of hydrogen yield is at 3wt% Platinum Alumina catalyst.

Effect of temperature has a great effect on the hydrogen yield. When the temperature for 3 wt% catalyst is increased from 210 deg C to 230 deg C, the hydrogen yield has increased 97% from 20.31 moles to 40.09 moles. The same type of graph also observed at concentration of catalyst at 1 and 5 wt%.

The optimum condition to produce maximum yield of hydrogen is at 230 deg C and 3wt% of catalyst concentration. For catalyst characterization, we only focused on catalyst sizes of fresh catalyst and spent catalyst. Based on the result there is no significant change to catalyst size and it eliminate the probable cause of the loss of  $H_2$  chemisorptions of the spent catalyst due to loss of Pt.



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# List of Abbreviation

APR	Aqueous-phase reforming
WGS	Water-gas shift
GC	Gas chromatography/chromatograph
TGA	Thermogravimetric analysis
PID	Proportional-Integral-Derivative
TCD	Thermal conductivity detector
FID	Flame ionization detector
ppm	parts per million
FESEM	Field Emission Scanning Electron Microscope

# 1. Introduction

# 1.1 Background

Fossil fuel is one of the sources that have been use since the start of civilization and that have been estimated that the uses of fossil fuel is equivalent to the same amount of energy we receive every 30 days from the sun. Fossil fuels are one of the non-renewable sources and will eventually run out because people are using them much faster than they can be restored within the earth. Burning fossil fuels produces photochemical pollution from nitrous oxides, and acid rain from sulphur dioxide. Burning fuels also produce greenhouse gases including vast amounts of carbon dioxide that may be causing the phenomenon of global warming that the planet is currently experiencing.

The recent increase in the price of fossil fuel as well as the awareness of global warming has created and emphasis on obtaining alternative fuels and energy from renewable source. Alternative fuels, also known as farts or advanced fuels, are any materials or substances that can be used as fuels, other than conventional fuels.



**Figure 1: Well Known Alternative Fuels** 

*GLUCOSE* also known as grape sugar, blood sugar, or corn sugar, is an important carbohydrate in biology. Cells use it as a source of energy and metabolic intermediate. Glucose is one of the main products of photosynthesis and starts cellular respiration in both prokaryotes (bacteria and archaea) and eukaryotes (animals, plants, fungi, and protists). Starch and cellulose are complex sugars and polymers of glucose (McMurry, John E., 1988). Nowadays scientists have found that besides using glucose in food industries, glucose also have a potential to be used in producing or obtaining an alternative fuels to replace non renewable sources. The alternative fuels that can be obtained from glucose are *HYDROGEN*.



Figure 2: Biomass to Hydrogen via the APR Process

Hydrogen gas has been suggested as a promising alternative to fossil fuels as an energy carrier for transportation needs. Hydrogen gas has a high energy capacity per unit mass (118.2 kJ g-1), and CO<sub>2</sub> is released during its combustion in conventional engines. However, most hydrogen is usually produced from stored methane reserves and other nonrenewable materials, resulting in net increases of CO<sub>2</sub> in the



environment. Shifting a fossil fuel economy to a hydrogen economy offers few environmental advantages if both are based on the net consumption of fossil fuels. Thus, it is essential for reducing  $CO_2$  emissions that hydrogen production not release a net amount of  $CO_2$  into the atmosphere and that the technologies and materials used to produce hydrogen are sustainable (Walid M. Alalayah, 2009).



Figure 3: Intermediate Products of the APR Process

There are many ways to convert from glucose to hydrogen production. These includes pyrolysis, steam gasification, microbial conversion, catalytic steam reforming and last but not least **Aqueous Phase Reforming**. The APR process is greenhouse-gas neutral, because the  $CO_2$  by-product that accompanies the H<sub>2</sub> is consumed by biomass growth and it is best suited for micro scale reforming due to simplicity of design and minimal waste handling issues. In addition to utilizing renewable feed-stocks, the APR process eliminates the need to vaporize water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen.



Figure 4: Process of Converting Glucose to Hydrogen

Hydrogen has been identified as a very attractive energy carrier (Kamili 2004). Hydrogen fuel cells are highly efficient device for the production for the electrical power. The only waste product from hydrogen fuel cells are water and heat. However, the technology in hydrogen production now is still not energy and cost efficient. Commercial technology for hydrogen production is via steam reforming of non renewable fossil fuels. However, the full environment benefit of moving toward a hydrogen society is realized when hydrogen is produced from renewable sources (Norbeck 1996).

## 1.2 Objective

Aqueous-phase reforming is a promising and attractive technology for hydrogen production from biomass considering its much lower energy requirement and the possibility of utilizing bio material in its wet form. The bio material used in the study was Glucose. This study was aimed at determining the effect of temperature and concentration of  $Pt/Al_2O_3$  on the hydrogen production as well as overall gas evolution of glucose APR.

The main objective of this research is to carry out a study on hydrogen production via aqueous phase reforming of *Glucose*. In this research, the effect of temperature and variation weight of catalyst will be investigated. Consequently, a process will be developed to produce the hydrogen at its maximum yield.

The specific objectives are:

- To study and optimize existing method in converting *glucose* to hydrogen.
- To study effect of
  - Temperature and
  - Catalyst concentration.
- To determine optimize amount of hydrogen produce via aqueous phase reforming of *GLUCOSE* by using High Pressure CSTR.

It is anticipated that the results of this could further enhance our understanding of the aqueous phase reforming process and its applicability to biomass. Ultimately, the objective of this study is to contribute to the body of knowledge that could help develop a solution to averting future energy crisis that might not be too-farfetched when the non-renewable fossil fuels resources of the world are finally depleted.



## 1.3 Sequence of Stages to Achieve Objective

The first phase of this project was the literature review on methods currently used in hydrogen production from *glucose*. From literature review, aqueous phase reforming was selected due to its advantages of low temperature and pressure in hydrogen production. Studies were done on the catalyst to be used and the calculation on the amount of reactant that need to be used.

The next phase started by conducting calibration of the equipment of the **HIGH PRESSURE REACTOR** and also **GAS CHROMATOGRAPHY**. After the calibration, the preliminary test will be conducted based on literature review. Finally, test run or experiment with varying process parameter including catalyst concentration and temperature. The result then be analyzed and its conversion factor will be calculated. The optimum parameter could then be determined.



# 2. Literature Review

## 2.1 Glucose

Glucose ( $C_6H_{12}O_6$ ) contains six carbon atoms, one of which is part of an aldehyde group. Therefore glucose is an aldohexose. In solution, the glucose molecule can exist in an open-chain (acyclic) form and a ring (cyclic) form (in equilibrium). The cyclic form is the result of a covalent bond between the aldehyde C atom and the C-5 hydroxyl group to form a six-membered cyclic hemiacetal. At pH 7 the cyclic form is predominant. In the solid phase, glucose assumes the cyclic form. Because the ring contains five carbon atoms and one oxygen atom (like pyran), the cyclic form of glucose is also referred to as glucopyranose. In this ring, each carbon is linked to a hydroxyl side group with the exception of the fifth atom, which links to a sixth carbon atom outside the ring, forming a CH<sub>2</sub>OH group. Glucose is commonly available in the form of a white powder or as a solid crystal. It can also be dissolved in water as an aqueous solution. Its solubility level is very high. (K.murphy, June 2007)



a) Chemical Structure of Glucose



b) 3D model of Glucose

Figure 5: Chemical structure of Glucose

# 2.2 Application of Hydrogen

Hydrogen is a clean and efficient energy and widely accepted as a potential substitute for fossil fuels. Biological hydrogen production stands out as an environmentally harmless process carried out under mild operating conditions, using renewable resources ([Koku and Eroğlu, 2002] and [Fan and Zhang, 2006]). Hydrogen finds use in diverse applications covering many industries. Below are the applications of hydrogen in industries.

- a) Fuel Cells ... used as a fuel to power fuel cell generators that create electricity through an electrochemical process in combination with oxygen.
- b) Food ... to hydrogenate liquid oils (such as soybean, fish, cottonseed and corn), converting them to semisolid materials such as shortenings, margarine and peanut butter.
- c) Chemical processing ... primarily to manufacture ammonia and methanol, but also to hydrogenate non-edible oils for soaps, insulation, plastics, ointments and other specialty chemicals.
- d) Metal production and fabrication ... to serve as a protective atmosphere in high-temperature operations such as stainless steel manufacturing; commonly mixed with argon for welding austenitic stainless. Also used to support plasma welding and cutting operations.
- e) Pharmaceuticals ... to produce sorbitol used in cosmetics, adhesives, surfactants, and vitamins A and C.
- f) Aerospace ... to fuel spacecraft, but also to power life-support systems and computers, yielding drinkable water as a by-product.

- g) Electronics ... to create specially controlled atmospheres in the production of semiconductor circuits.
- h) Petroleum Recovery and Refinery ... to enhance performance of petroleum products by removing organic sulfur from crude oil, as well as to convert heavy crude to lighter, easier to refine, and more marketable products. Hydrogen's use in reformulated gas products helps refiners meet Clean Air Act requirements.
- Power Generation ... to serve as a heat transfer medium for cooling high speed turbine generators. Also used to react with oxygen in the cooling water system of boiling water nuclear reactors to suppress intergranular stress corrosion cracking in the cooling system.

# 2.3 Existing method in Hydrogen Production

There are many ways to convert glucose to hydrogen production, there are:-

- Pyrolysis,
- Steam gasification
- Microbial conversion
- Catalytic steam reforming and
- Aqueous phase reforming

The following section will discuss about the technique used in extracting hydrogen from Glucose

## 2.3.1 Pyrolysis

Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Lower process temperature and longer vapour residence times favour the production of charcoal. High temperature and longer residence time increase the biomass conversion to gas and moderate temperature and short vapour residence time are optimum for producing liquids. Fast pyrolysis for liquids production is of particular interest currently.

Fast pyrolysis occurs in a time of few seconds or less. Therefore, not only chemical reaction kinetics but also heat and mass transfer processes, as well as phase transition phenomena, play important roles. One way this objective can be achieved is by using small particles, for example in the fluidized bed processes. Another possibility is to transfer heat very fast only to the particle surface that contacts the heat source.

The process of pyrolysis is endothermic, requiring a substantial heat input to raise the biomass to reaction temperature, although the heat of reaction is insignificant. Heat transfer in commercial reactors is a significant design feature. Figure 6 summarizes the main methods of providing the necessary heat.



Pyrolysis typically occurs under pressure at operating temperature above  $430^{\circ}$ C. Pyrolysis processes yield liquids fuels at low temperature ( $400-600^{\circ}$ C) and gaseous products at higher temperature (>750°C). Pyrolysis can be carried out in two ways; pyrolysis with and without any carrier gas nitrogen (N<sub>2</sub>).

## 2.2.2 Steam Gasification

The Energy Efficiency and Renewable Energy (EERE) agency of the US DOE defines biomass gasification to be a process whereby "biomass is converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds by applying heat under pressure in the presence of steam and a controlled amount of oxygen (in a unit called a gasifier)". Temperature for gasification is generally higher (> 600°C – 700°C) than that used for pyrolysis. Unlike pyrolysis, gasification may proceed in the presence of some O<sub>2</sub> or steam. Supercritical water gasification (SCWG), including near subcritical ones are also being investigated. Catalysts are added to the process to lower operating temperatures. The gaseous products are usually composed of H<sub>2</sub>, CO, CO<sub>2</sub> and possibly some alkanes.

Modell pioneered the treatment of biomass in supercritical water. First, he studied glucose gasification at subcritical (T = 150, 200, 300°C) conditions. He reported that the process produced gas, liquid and solid by-products, with 40% of the carbon feed in the solid product at 300°C and 0.3% in the gas. He further noted that increasing the temperature from 150° to 300°C, the amount of char also increased. However, when supercritical conditions (T = 374°C and P = 218 atm) were used, no char was formed. From a set of experiments, it was shown that maintaining the density of water, that is, maintaining the supercritical pressure as well as the temperature, was necessary so that no char would be formed. Such was the case also for cellulose and for maple sawdust. It was the first time that char was not formed during heat treatment of biomass. In the SCWG of maple sawdust in the absence of a catalyst, the highest H<sub>2</sub> percentage was 18% (CO was the major gas component) after 15 minutes of reaction time. Though he varied the reaction time in five runs, it was difficult to conclude as to the effect of time with H<sub>2</sub> production since the amount of carbon



in the feed was varying. In the presence of catalyst, his glucose gasification recorded a highest percentage of 45%  $H_2$  after 30 minutes of reaction in the presence of seven mixed catalysts: five of which are Ni-based, and then Pt/Al<sub>2</sub>O<sub>3</sub> and Co/Mo catalyst (Frédéric Vogel, 2005).

#### 2.2.3 Microbial Conversion

Microorganism Enterobactera erogenes HU-101, isolated as a high-rate  $H_2$  producer from methanogenic sludge, can convert various carbohydrates such as sugars and sugar alcohols, to  $H_2$ , ethanol, 2,3-butanediol, lactate and acetate.  $H_2$  can be biologically produced either by photosynthetic microorganism or fementative anaerobes. Ito et al (2005) studied  $H_2$  production using E. aerogenes as it exhibits uninhibited growth in an atmosphere of 100%  $H_2$ . During the studies, they found that E. aerogenes HU-10l mainly produce  $H_2$  and ethanol with a minimal production of other by-product when glucose was used as the substrate.

#### 2.2.4 Catalytic Steam Reforming

Catalytic steam reforming of organic compounds is one of the processes used to produce hydrogen. Catalyst is mainly used to increase the reaction rate and to increase the selectivity of hydrogen. Steam reforming reactions of oxygenated organic compounds such as glycerol and glucose proceeds according to the following equation 2.1 (Czernik et al., 2002):

$$C_{n} \underset{m}{H} \underset{m}{O}_{k} + (n-k) \underset{2}{H} \underset{2}{H} O \leftrightarrow nCO + [(n+m/2-k)] \underset{2}{H} \underset{2}{H}$$
(2.1)



Because of the excess steam used in the process, carbon monoxide further undergoes the water gas shift reaction to produce  $CO_2$  and  $H_2$ . Research has been also carried out to produce hydrogen from biomass-derived oxygenated compounds such as methanol and ethylene glycol using catalytic aqueous phase reforming reactions (Davda et al., 2003).

Czernik et al. (2000) carried out catalytic steam reforming of bio oil derived fractions and crude glycerine (a by-product from transesterification of vegetable oil with methanol) using a fluidized bed reactor to produce hydrogen. In experiments, 150g - 200g of a commercial nickel based catalyst was used. Catalyst was fluidized by the superheated steam. They reported that crude glycerine was a very viscous liquid and partially miscible with water. The temperature of crude glycerine was maintained at 60-80 °C because of its high viscosity. They suggested that at a lower viscosity, it was easier to pump and atomize. The glycerine was fed at the rate of 78g/h, GHSV = 1600  $h^{-1}$  and steam at a rate of 145 g/h. Therefore, the steam to 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 parts per million (ppm) to 2200ppm when the run time increased from 0 min to 250 min. The hydrogen yield was around 77wt%. They suggested that a higher yield of hydrogen would be possible if a higher amount of steam was used in the process. Conversion of carbon monoxide in the gas through water-gas shift to  $CO_2$  and  $H_2$  would increase the yield to 95 wt %. These results showed that a commercial value byproduct from bio-diesel production could become a viable renewable material for producing hydrogen. They suggested that integration of the water-gas shift reaction and fluidized bed technologies would enhance the production of hydrogen and make it economically feasible.

Sugar-containing hydrolysates and glycerol-containing liquors derived from residual fats can also be potential feedstock for the production of hydrogen



(Chornet and Czernik, 2002). Chronet and Czernik, (2002) suggested that feedstocks should preferably be obtained from high-productivity biomass crops (for example, jatropha plant can grow even in dry land); with little or no use of synthetic fertilizers (fertilizers could act as a catalyst in the process). They suggested that the steam reforming of biomass derived oxydegenated hydrocarbon such as glycerol, sorbitol and ethylene glycol using platinum alumina steam reforming catalyst could maximize the production of hydrogen.

Steam reforming offers an efficient, economical, and widely used process for hydrogen production, and provides near- and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65% to 75%, among the highest of current commercially available production methods. Natural gas is a convenient, easy to handle, hydrogen feedstock with a high hydrogen-to-carbon ratio. It is also widely available from sources in the U.S. and Canada. The cost of hydrogen produced by Steam Reforming is acutely dependant on feedstock prices and is currently the least expensive among all bulk hydrogen production technologies.

#### 2.2.5 Aqueous phase reforming (APR)

Cortright et al. (2002) carried out aqueous-phase reforming of sugars and alcohols using a fixed-bed reactor at temperatures near  $265^{\circ}C$  and  $225^{\circ}C$  to produce hydrogen. They used platinum catalyst supported on nanofibres of  $\gamma$ -alumina. Alcohols such as glycerol, sorbitol, methanol and ethylene glycol were used in this study. They suggested that the reforming of more immediately available compounds such as glucose is likely to be more practical. Higher hydrogen yields were obtained using sorbitol, glycerol and ethylene glycol as a feed molecule for aqueous-phase reforming than the hydrogen yield from glucose. The hydrogen yield from glucose reforming was 64.8mol% and 57mol% at  $225^{\circ}C$  and  $265^{\circ}C$  respectively. They found that gaseous streams



from aqueous phase reforming of the oxygenated hydrocarbons contained low levels of carbon monoxide (<300 ppm). Liquid products from the reactions essentially consisted of ethanol, 1,2-propanediol, ethanol, 1-propanol, acetic acid, ethylene glycol, acetaldehyde, 2 propanol, propionic acid, acetone, propionaldehyde and lactic acid.

With the report of Dumesic et al. (University of Wisconsin-Madison) of the aqueous-phase reforming (APR) process in 2002, the possibility of producing hydrogen at much lower temperatures than either gasification or pyrolysis was demonstrated. From the typical gasification temperature of above 500°C, APR was shown to be capable of producing  $H_2$  at around 500K (227°C) using oxygenate model compounds such as ethylene glycol. In the presence of a suitable catalyst such as platinum, APR is anchored on two important  $H_2$ -generating reactions: reforming and water gas shift (WGS).

$$C_m H_n O_m \leftrightarrow m CO + n/2 H_2 \qquad (Reforming)$$

$$CO + H_2 O \leftrightarrow CO_2 + H_2 \qquad (WGS)$$

In their first article published in *Nature*, the group of Dumesic reported that APR of methanol and ethylene glycol could have as high as 96%  $H_2$  selectivity while the more "oxidized" glucose only had a selectivity of 50%. They concluded that the ratio of oxygen to hydrogen in the molecule affects hydrogen selectivity – the more reduced the molecule, the better is its  $H_2$  selectivity with APR. The authors accounted for this finding by noting the comparative likelihood of breaking a C-C bond and C-O bond on the metal catalyst used. The first occurrence will form the desired product (i.e.  $H_2$ ) while

the latter will cause formation of alkanes or dehydrated oxygenates. These proposed mechanisms are illustrated in Figure 7.



Figure 7: Possible pathways of competing bond breaking on Pt. (a) C-C bond breakage leading to formation of H2 and CO. (b) C-O bond breakage leading to formation of alkane/dehydrated molecule through reaction of intermediate with hydrogen.

In order to increase the selectivity from glucose, Davda and Dumesic developed a two-stage system consisting of a hydrogenation reactor coupled to a reforming reactor. In the hydrogenation reactor, the glucose feed stream was reacted with  $H_2$  to form sorbitol. After this, the stream was directed onto the reforming reactor where APR occurred. From an initial  $H_2$  selectivity of 10.5%, they were able to increase the selectivity to 62.4% by incorporating the hydrogenation reaction.



Ideally, the metal catalyst used in the process should catalyze both of the aforementioned reactions. Before the group started using bimetallic catalysts,  $Pt/Al_2O_3$  was identified to have the highest hydrogen selectivity. They have studied APR of ethylene glycol and methanol using platinum and the less expensive Sn-Ni catalysts on different supports (acidic, basic and neutral) and found that  $Pt/Al_2O_3$  by far gave the best selectivity among the catalysts. Addition of Sn on Ni was found to lower methanation on Ni and thus increase hydrogen selectivity. Recently, Huber et al. applied bimetallic Pd and Pt catalysts on ethylene glycol APR. Using a high-through-put reactor, they were able to screen more than 130 bimetallic catalysts. After identifying the promising ones, they then subjected these to flow reactor APR conditions with ethylene glycol. Results showed that combining  $PtFe_9/Al_2O_3$  gave TOF values that are three times higher than  $Pt/Al_2O_3$ . This increase was much higher for Pd. TOF for  $PdFe_9/Al_2O_3$  were 39-46 times higher  $Pd/Al_2O_3$  at the same reaction conditions.

Aqueous-phase reforming (APR) produces hydrogen from biomass-derived oxygenated compounds such as glycerol, sugars and sugar alcohols. APR is unique in that the reforming is done in the liquid phase.

The process generates hydrogen without volatilizing water, which represents major energy savings. Furthermore, it occurs at temperatures and pressure where the water-gas shifts reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor. By taking place at low temperatures, the process also minimizes undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures. In another mode, the reactor and catalysts can be altered to allow generation of high-energy hydrocarbons (propane, butane) from biomass-derived compounds. The APR process is greenhouse-gas neutral, because the  $CO_2$  byproduct that accompanies the  $H_2$  is consumed by biomass growth. In addition to utilizing renewable feed-stocks.



Figure 8: The APR Process



Figure 9: Method of extracting Hydrogen from Glycerol



The APR process offers a number of costs and efficiency benefits (George W. Huber, 2005):

- It generates hydrogen without the need to produce high-temperature steam, which represents a major energy saving over other multi-step processes for the generation of hydrogen from hydrocarbons;
- APR generates about 15 times more hydrogen per mass of catalyst than existing steam reforming process.
- It occurs at temperatures and pressures where the water-gas shift reaction is favorable,
- It occurs at pressures (typically 15 to 50 bar) where the hydrogen-rich effluent can be effectively purified,
- It takes place at low temperatures that minimize undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures;
- It uses widely available bio feedstocks or by products of other biofuel processing (i.e., the glycerin produced from the biodiesel production process.



# 3. Methodology

This section will describe the experimental technique, apparatus used, as well as the analytical method undertaken in the course of this study to achieve the objective mentioned previously. Procedures and experimental details of each phase of the research are described in this section.



Figure 10: Flow chart of methodology

# 3.1 Experiment Condition

The objective of this research is to study the effect temperature and catalyst concentration in the reactor with a constant pressure, reaction duration and feed concentration. A qualitative analysis using gas chromatography will then be performed for the produce gas from the reaction. From the result and observation from the experiment, an optimum condition for hydrogen production then will be defined. For this experiment, the author will use glucose as the feedstock to obtain the result.

## 3.2 Glucose Feed Condition

The reforming process is a reversible process. Hydrogen produce from the reaction could be reacted again to form back glucose. Therefore, by increasing the concentration of water, it could encourage the forward path of the reaction, promoting a more complete reaction from glucose to hydrogen. In order to compare the hydrogen yield against other parameter, the glucose feed concentration is determine to be at 10 wt%.

## 3.3 Temperature Control

The temperature throughout the experiment is crucial for the selectivities for production of hydrogen. A low temperature might result in incomplete reaction. If the temperature is too high, it might cause dissociation of the reaction product to further react to form unwanted by-product. Therefore, it is important to know the optimal temperature where highest hydrogen yield can be obtained. The author decided to make temperature varies at 210 deg C, 220 deg C and 230 deg C.

# 3.4 Type of catalyst use

The first reports concerning glucose reforming appeared in the pioneering work of the group of Dumesic. They considered hydrogen production, for example, from glucose at temperatures near 500 K in a single-reactor aqueous liquid phase reforming process. According to reaction, glucose is almost completely converted into CO<sub>2</sub> and H<sub>2</sub>. Major steps in the reaction include the dehydrogenation of glucose on the metal surface with the formation of adsorbed intermediates before cleavage of C-C and C-O bonds. Subsequent C-C bond breaking leads to H<sub>2</sub> and CO, while CO reacts with water according to the water-gas shift reaction. An effective catalyst thus breaks C-C, O-H, and C-H bonds in the glucose reactant without cleaving C-O bonds or hydrogenating CO or CO<sub>2</sub> to form alkanes (Dumesic, 2005). Many metals on various supports have been evaluated in high-throughput mode. Pt on alumina and Sn-doped Ni on alumina have been found most valuable. Somewhat higher H<sub>2</sub> and CO selectivities were reported when reforming catalysis is carried with Platinum Alumina. Therefore in this project, the author decided to use Platinum Alumina as a catalyst.

## 3.5 Concentration of catalyst

Based on catalyst that the author has decided, this project is further investigated by varying catalyst concentration. The concentrations of catalyst used are 1 wt%, 3 wt% and 5 wt% and the mass of catalyst calculated as per table below.

Catalyst Concentration (wt %)	Mass of catalyst (g)
1	3.00
3	9.00
5	15.00

Table 1: Mass of catalyst of Platinum Alumina

# 3.6 Apparatus Use

Experiment of hydrogen generation will be conducted using lab scale high pressure CSTR that available at Block 3, level 2, University Technology PETRONAS. A 1000-mL stainless steel High Pressure Reactor was used for all the runs in this study. The assembly included a magnetic drive for the mechanical stirrer and a temperature controller with a PID controller and J-type thermocouple. The reactor was outfitted with a gas collector at the top reactor head. Lastly, a check valve was attached at the end to contain and control gas sample exit from the sample volume. Diagrams and a picture of the reactor are presented below.



Figure 11: High pressure reactor assembly. (a) Top assembly (valve for liquid sampling not included; actual pressure gauge much larger); (b) bottom bomb



The samples were taken using Tedler gas bag. Two modes of sampling were done during the research. In the early part of the study, intermittent sampling was done every 30 minutes. However, the disturbance this method caused to the system precluded from having good reproducibility. As such, sampling was then done by extracting the gas product when the temperature of the reactor same with room temperature.

The Glucose, water and catalyst will be weight separately based on calculation. This is one of the important steps to ensure the chemical reaction between the Glucose and water was done in complete reaction process based on theoretical calculation done. After completing the experiment based on certain parameters that have been decided, the gas will be collected by using 0.5L Tedler gas bag. This gas will then send to another lab to analyze the composition of product gases by using Gas Chromatography (GC) Agilent G 1540A.

Gas Chromatography is use to analyze composition. The GC was equipped with flame ionization detector (FID) and thermal conductivity reactor (TCD). FID is use to detect common hydrocarbon gases such as methane (CH<sub>4</sub>), carbon monoxide (CO), ethylene ( $C_2H_4$ ), ethane ( $C_2H_6$ ) and acetylene ( $C_2H_2$ ) while TCD is use to detect hydrogen ( $H_2$ ), oxygen ( $O_2$ ), nitrogen ( $N_2$ ), Carbon dioxide (CO<sub>2</sub>) and Carbon Monixide (CO).

# 3.7 GC Calibration

Before conducting the analysis, Gas chromatography will be calibrated. A certified gas mixture from Airgas was used to calibrate the GCs used in this study. The mixture contained: 25.50%  $H_2$ , 4%  $C_2 H_6$ , 3%  $CO_2$ , 2% CO, 1.02%  $CH_4$  and the balance  $N_2$ . Calibration of the GC required injecting different concentrations of a certain gas and recording the corresponding area units as reported by the data software. Various concentrations were prepared by mixing different flowrates of the gas mixture and pure helium. Calibration of air in the GC was also done to check for contamination due to unavoidable leaks.

# 3.8 Spent Catalyst Characterization

Catalyst stability is an important consideration for reactions that involve catalysts – especially those that use expensive metal catalysts. With this in mind, the spent catalyst was characterized using elemental analysis by using **Field Emission Scanning Electron Microscope (FESEM).** This analysis will be focused on particle size of fresh and spent catalyst. Samples of fresh catalyst pellets as well as spent ones were sent to technician for elemental analysis where the particle size will be determined.

# 4. Result and Discussion

From experimental technique that have been discussed in methodology, all result will be recorded and analyze. An attempt to give meaning and relevance to these data in the context of the objectives of the study is also presented. Based on result and observation the optimum condition for hydrogen yield will be determined. Based on previous planning, we decided to conduct the preliminary test before proceeding to real test run based on parameter that have been discuss in literature review.

 $C_6H_{12}O_6 \leftrightarrow 6H_2 + 6CO$ 

## 4.1 Experiment Result and Observation

Experiment result shown that hydrogen is produced from APR of glucose. From the chemical reaction above, it can be seen that each mol of glucose contains 12 moles of Hydrogen. From literature review, APR involve two reaction in producing hydrogen, one is the reaction above that is Low Temperature Reforming and another one is Water Gas Shift below:

$$6CO+ 6H_2O \leftrightarrow 6H_2 + 6CO_2$$

Hence overall, there are a total of 12 moles of hydrogen produce in APR method as shown below

$$C_6H_{12}O_6 + 6H_2O \leftrightarrow 12H_2 + 6CO_2$$

In standard dry air, the gas consists of only 0.5 ppm hydrogen gas as shown in Table 2, while Table 3 showed composition of product gas of APR experiment at different temperature and catalyst concentration.

Gas	Chemical Symbol	% by Volume	% by Weight	Ppm (by Volume)
Nitrogen	N2	78.08	75.47	780805
Oxygen	02	20.95	23.2	209450
Argon	Ar	0.93	1.28	9340
Carbon Dioxide	CO <sub>2</sub>	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	H2	0.00005	Negligible	0.5
Xenon	Хе	8.7 exp -6	0.00004	0.087

Table 2: Standard Composition of Dry Air

Fe	ed	Temperature	Durations	Compositior	n of product G	as (mole %)	
Glucose wt%	Catalyst wt%	(deg C)	(deg C)	(min)	H2	со	CO2
10	1	210	90	23.34745	2.14959	5.03497	
10	1	220	90	45.18448	1.63580	4.68876	
10	1	230	90	67.45679	2.83737	4.98736	
10	3	210	90	40.62417	2.65438	4.16660	
10	3	220	90	62.59685	2.83315	5.03258	
10	3	230	90	80.18817	1.11391	3.68584	
10	5	210	90	30.34409	2.65736	5.42010	
10	5	220	90	58.56472	2.12764	3.79261	
10	5	230	90	76.01504	1.82161	2.94995	

#### Table 3: Composition of product gas of APR experiment at various parameters

The amount of glucose used in the experiment is 10wt%, which is equivalent to 0.166 moles. Based on complete reaction 0.166 mole glucose will produce 2.00 mol hydrogen. The hydrogen yield which is first reported in mol % is converted into mol to compare the conversion of glucose to hydrogen. Table 4 shows the amount of hydrogen produced and conversion factor.

Fe	ed			Hydrogen yield (mole)		
	ſ	Temperature	Durations		I	Conversion
Glucose	Catalyst	(deg C)	(min)	Theoretical	Experimental	Factor
wt%	wt%					
10	1	210	90	2.00	0.2334745	11.6737
10	1	220	90	2.00	0.4518448	22.5922
10	1	230	90	2.00	0.6745679	33.7284
10	3	210	90	2.00	0.4062417	20.3121
10	3	220	90	2.00	0.6259685	31.2984
10	3	230	90	2.00	0.8018817	40.0941
10	5	210	90	2.00	0.3034409	15.1720
10	5	220	90	2.00	0.5856472	29.2824
10	5	230	90	2.00	0.7601504	38.0075

# Table 4: Comparison of theoretical and experimental hydrogen yield and itsconversion factor

It is observed that the highest yield of hydrogen, which is 0.802mol had exhibit a conversion factor of 40.09%. This suggests that there are still 59.91% of hydrogen content in glucose is not converted into hydrogen gas. Instead, the hydrogen might have been converted into other form of hydrocarbon such as Methane.

Beside the main reason for the low conversion factor might be due to the selection of catalyst. Although platinum alumina exhibit highest water gas shift rate which produce the hydrogen from the reaction of water and carbon monoxide, it has show no activity for C-C bond breaking in the reforming.

# 4.2 Effect of Catalyst Concentration

The effect of catalyst concentration on hydrogen yield of glucose is shown in Figure 12. It is observed from the figure that the hydrogen yield behave like a parabolic curve with increases in catalyst concentration. For 90mins reaction, hydrogen yield increase by 18.87% from 0.6745679 moles at 230 deg C then decreases to 5.20% to 0.7601504 moles. The same pattern also showed at temperature of 210 and 220 deg C.

Since catalyst is used to increase the rate of reaction, the decrease of hydrogen yield at higher catalyst concentration is investigated. It is assumed that a certain level of deviation might occur during the experiment that causes the decrease of hydrogen production at 5wt% of catalyst. 3wt% might be the saturation point for the catalyst and any increase of catalyst might give a significant effect to hydrogen yield.

It also possible that too much of catalyst might cause the reaction to be over reacted and the produce hydrogen is dissociated to form other substances. It may combine with oxygen to reverse the APR process to form water.



Figure 12: Effect of catalyst concentration on hydrogen yield

# 4.3 Effect of Temperature

The increase of temperature of reaction has greatly affected the hydrogen yield. From figure 13, it is observed that by increasing the temperature at catalyst concentration of 3 wt% at 210 deg C to 230 deg C the hydrogen yield was increase by 97% from 20.31 moles to 40.09 moles. The same type of graph also observed at concentration of catalyst at 1 and 5 wt%.



Figure 13: Effect of temperature to Hydrogen yield



# 4.4 Characterization of catalyst



Figure 14: Describe the in-lens fresh catalyst (Left side) and spent catalyst (Right side)

From the data that we get from FESEM, elemental analysis of the spent  $Pt/Al_2O_3$  catalyst showed a basically unchanged Pt/Al ratio compared to that of the fresh catalyst. It also confirmed the presence of platinum in the catalyst after APR to nearly the same extent as the fresh catalyst as per shown in Table 5.

	Fresh Catalyst		Spent Catalyst		
	Wt%	No of atoms	Wt%	No of atoms	
Platinum	0.35	1.1 e21	0.33	1.0 e21	
Alumina	39.6	8.8 e23	38.7	8.6 e23	
Pt/Al	1.2 e-3		-	1.2 e-3	

Table 5: Platinum and aluminum content of fresh and spent Pt/Al2O3 catalyst

This therefore eliminates the probable causes, of the loss of  $H_2$  chemisorptions of the spent catalyst due to loss of Pt. It must be noted though that the ratio does not automatically imply that not even a small amount of platinum particles were lost in the process. It is possible that some catalyst particles were torn off due to abrasion during agitation of the mixture.

# 4.5 Summary of Result

Overall, it is found that maximum hydrogen yield is produced at 10 wt% feed concentration, 3 wt % platinum alumina catalyst concentration with 90 minutes time duration at 230 deg C. The yield of the hydrogen under this condition is 80.19 mole %. From the result we obtain, it can be observed that since the increase of catalyst does not increase the hydrogen yield significantly, it is more appropriate to use 3 wt% as this could reduce the cost of production.

# **5.** Conclusion

The results of this study show that hydrogen can be produced from glucose by using high pressure reactor at temperatures and pressure much lower than those methods currently used in hydrogen production processes and aqueous phase reforming studies shows that there is a potential for producing value added products from renewable sources such as glucose.

The parameters investigated in the project are the catalyst concentration and variation of temperature. The use of 3 wt% catalyst had increases the hydrogen yield for about 90% compared to 1wt%, while 5wt% catalyst shown a slight decrease in hydrogen yields. This could be caused by the errors occurred during the experimental works. A reverse reaction also might cause the decrement of hydrogen yield. Reaction at 230 deg C can produce more hydrogen than temperature at 210 deg C. The optimum condition to produce maximum yield of hydrogen is at 230 deg C and 3wt% of catalyst concentration. For catalyst characterization, we only focused on catalyst sizes of fresh catalyst and spent catalyst. Based on the result there is no significant change to catalyst size and it eliminate the probable cause of the loss of H<sub>2</sub> chemisorptions of the spent catalyst due to loss of Pt.

From the experiment conducted it shows that APR process is unique because it can produce hydrogen in liquid phase. It also generate  $H_2$  without volatizing water in which represent energy saving. It is foreseen that hydrogen generation fro glycerol has great potential for further development.



# 6. Recommendation

The experiments in this study were done using a High Pressure Reactor. A limitation of a High Pressure Reactor that the author use in this experiment is the stirrer of the reactor malfunction and affectted the result of this experiment because the catalyst that has been put inside the reactor will be settle down at the bottom of reactor. It will result to low Hydrogen gas yield. Thus for further studies of APR, by repairing the stirrer of the reactor might be will increase the hydrogen yield. We can also try to use another type of reactor such as continuous flow reactor that is expected to improve this condition. Indeed, the similar hydrogen yields between different substrates creates an expectation that biomass can attain yields that will be comparable to previous studies for glucose.

Aside from a change in reactor configuration, optimizing the system with respect to pressure, feed concentration as well as variation of duration time are expected to finetune the APR processing of Glucose. Energy balance on the APR system indicate that significant energy losses can occur because vaporization of water in the reactor system to maintain the partial pressure of water in the hydrogen gas bubble formed in the reactor. The thermal efficiency of the system can be improved by operating it with higher concentration of feedstock as for this experiment is glucose. As for duration time, since we varies the concentration of catalyst, it will be better to varies the time duration so that we can find the optimum duration time because of the purpose of catalyst is to increase reaction of rate. Aside from glucose, other biomass feeds with different chemical compositions may also be studied. Studying the kinetics of their hydrogen production through APR is expected to be a useful tool in evaluating the versatility of this process.

![](_page_45_Picture_0.jpeg)

#### Hydrogen Production Via Aqueous Phase Reforming Of Glucose

Lastly, analysis of the liquid by-products is considered to be a very important tool in developing a better understanding of the chemistries involved in the reactions. The apparent difference in the reactivity of glucose may then be explained. The importance of the hemiacetal functionality of glucose may then be better understood as this information is expected to have an implication in the ultimate decision of whether APR can be sustainably and cost-effectively applied to biomass for hydrogen production.

![](_page_46_Picture_0.jpeg)

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![](_page_47_Picture_1.jpeg)

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![](_page_48_Picture_0.jpeg)

# 8. Appendices APPENDIX A

#### **Calculation of reactant mass**

#### **Table 6: Molar Mass of Substance**

Reactant	Chemical Formula	Molar Mass (g/mol)
Glucose	C6H12O6	180.16
Water	H2O	18.015

 $C_6H_{12}O_6 + 6H_2O \leftrightarrow 12H_2 + 6CO_2$ 

**Based on reaction above:** 

**Total mass of reactant** 

=<u>300.00g</u>

#### For 10wt% of feed concentration

Mass of glucose use,

=feed concentration x mass of reactant

= (10/100) x 300.00

=<u>30.00g</u>

Mass of water,

=Mass of reactant – mass of glucose

=300.00 - 30.00

=<u>270.00g</u>

#### **Calculation for catalyst Platinum Alumina**

For 1wt% catalyst concentration

 $= (1/100) \times 300.00$ 

= <u>3.00g</u>

For 3wt% catalyst concentration

- = (3/100) x 300.00
- = <u>9.00g</u>

For 5wt% catalyst concentration

= (5/100) x 300.00

= <u>15.00g</u>

The preliminary test has been successfully conducted and proceeds to real test run.

#### **Theoretical mol hydrogen produce**

Mol of Glucose	= Mass / Molar Mass		
	= 30 / 180.16		
	= 0.1665 mol		

Based on equation from 1 mol of Glucose it will produce 12 mol of hydrogen

Theoretical mol hydrogen produce = 12 x 0.1665 = 2.00 mol

![](_page_50_Picture_0.jpeg)

## **APPENDIX B**

## **Result Sheet Sample**

	:				
Mass of Glu	Mass of Glucose (g) = Actual =				
Mass of Wa	s of Water (g) = Actual =				
Catalyst					
Mass of catalyst (g) = Actual =					
Temperatur	e (°C) = 220 °C				
Initial Pressu	ure (psi) = 50psi				
Time (Minute)	Reactor Temperature (°C)	Reactor Pressure (psi)	Remarks		

![](_page_51_Picture_0.jpeg)

## Figure 15: Result Sheet Sample

### Table 7: GC Result

Parameter <u></u>	Result			
Feed Concentration: 10wt%	Area Amt/Area [25 uV*s]	Amount Grp Name [mol8]		
Catalyst Concentration: 1wt% Reaction Duration: 90 minutes Temperature: 210 deg C Pressure: 5 Bar	1404.40820 3.58512e-3 121.55010 1.92081e-3 552.98956 3.88722e-3	3       5.03497       Carbon dioxide         1       23.34745       Hydrogen         -       Methane         3       2.14959       CO         30.53201       30.53201		
Feed Concentration: 10wt% Catalyst Concentration: 1wt% Reaction Duration: 90 minutes Temperature: 220 deg C Pressure: 5 Bar	Area Amt/Area [25 uV*s] 1307.83972 3.58512e-3 235.23677 1.92081e-3 420.81430 3.88722e-3	Amount Grp Name [mol8] 		

![](_page_52_Picture_0.jpeg)

Feed Concentration:	Area Amt/Area Amount Grp Name
10wt%	[25 uV*s] [molts]
Catalyst	1391.12903 3.58512e-3 4.98736 Carbon dioxide 351.18954 1.92081e-1 67.45679 Hydrogen
Concentration: 1wt%	729,92352 3.88722e-3 2.83737 CO
Reaction Duration: 90	75.28152
minutes	
Temperature: 230 deg	
C Dragoura: 5 Dar	
Flessule. 5 Dai	
Feed Concentration:	
10wt%	Area Amt/Area Amount Grp Name [25 uV*s] [mol%]
Catalyst	1152 19335 3 58512e-3 4.16660 Carbon dioxide
Concentration: 3wt%	211.49515 1.92081e-1 40.62417 Hydrogen
Reaction Duration: 90	682.84729 3.88722e-3 2.65438 CO
minutes	47.44515
minutes Temperature: 210 deg	47.44515
minutes Temperature: 210 deg C	47.44515
minutes Temperature: 210 deg C Pressure: 5 Bar	47.44515
minutes Temperature: 210 deg C Pressure: 5 Bar	47.44515
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration:	47.44515 Area Amt/Area Amount Grn Name
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt%	47.44515 Area Amt/Area Amount Grp Name [25 uV*s] [mol%]
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt% Catalyst	47.44515 Area Amt/Area Amount Grp Name [25 uV*s] [mol%] [[[
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt% Catalyst Concentration: 3wt%	47.44515 Area Amt/Area Amount Grp Name [25 uV*s] [mol%] [
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt% Catalyst Concentration: 3wt% Reaction Duration: 90	47.44515 Area Amt/Area Amount Grp Name [25 uV*s] [mol%] 1403.74304 3.58512e-3 5.03258 Carbon diox 325.88800 1.92081e-1 62.59685 Hydrogen Methane 728.83771 3.88722e-3 2.83315 C0
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt% Catalyst Concentration: 3wt% Reaction Duration: 90 minutes	Area       Amt/Area       Amount       Grp       Name         [25 uV*s]       [mol%]         1
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt% Catalyst Concentration: 3wt% Reaction Duration: 90 minutes Temperature: 220 deg	47.44515 Area Amt/Area Amount Grp Name [25 uV*s] [mol%] 
minutes Temperature: 210 deg C Pressure: 5 Bar Feed Concentration: 10wt% Catalyst Concentration: 3wt% Reaction Duration: 90 minutes Temperature: 220 deg C	47.44515 Area Amt/Area Amount Grp Name [25 uV*s] [mol8] [[

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![](_page_53_Picture_0.jpeg)

Feed Concentration: 10wt% Catalyst Concentration: 3wt% Reaction Duration: 90 minutes Temperature: 230 deg C	Area [25 uV*s] 1028.09460 417.47092 286.55652	Amt/Area 3.58512e-3 1.92081e-1 - 3.88722e-3	Amount [mol8] 3.68584 80.18817 1.11391 84.98792	Grp Name Carbon dioxide Hydrogen Methane CO
1 1055u10. J Dal				
Feed Concentration: 10wt% Catalyst Concentration: 5wt% Reaction Duration: 90 minutes Temperature: 210 deg C Pressure: 5 Bar	Area [25 uV*s]  1511.83191 157.97559 683.61572	Amt/Area 1	Amount [mo18] 5.42010 30.34409 2.65736 38.42154	Grp Name Carbon dioxide Hydrogen Methane CO
Feed Concentration: 10wt% Catalyst Concentration: 5wt% Reaction Duration: 90 minutes Temperature: 220 deg C Pressure: 5 Bar	Area [25 uV*s] 1057.87488 304.89621 - 547.34229	Amt/Area 3.58512e-3 1.92081e-1 3.88722e-3	Amount [mol%] 3.79261 58.56472 2.12764 64.48497	Grp Name Carbon dioxide Hydrogen Methane CO

![](_page_54_Picture_0.jpeg)

Hydrogen Production Via Aqueous Phase Reforming Of Glucose

Feed Concentration: 10wt%	Area [25 uV*s]	Amt/Area	Amount [mol%]	Grp Name
Catalyst				
Concentration: 5wt%	822.83276 395.74500	3.58512e-3 1.92081e-1	2.94995	Hydrogen
<b>Reaction Duration: 90</b>		-	-	Methane
minutes	468.61530	3.88722e-3	1.82161	co
Temperature: 230 deg			80.78660	
С				
Pressure: 5 Bar				

![](_page_55_Picture_0.jpeg)

Hydrogen Production Via Aqueous Phase Reforming Of Glucose

![](_page_55_Picture_3.jpeg)

![](_page_55_Picture_4.jpeg)

**High Pressure Reactor** 

![](_page_55_Picture_6.jpeg)

Weighing water

![](_page_56_Picture_1.jpeg)

Hydrogen Production Via Aqueous Phase Reforming Of Glucose

![](_page_56_Picture_3.jpeg)

Gas Bag that have been use to take gas sample after completed test run

![](_page_56_Picture_5.jpeg)

Picture taken during test run