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Methane recovery from manure biogas using amine absorption for hydrogen synthesis by tubular steam reforming

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Abstract

Since the beginning of the industrial revolution in the 18th century, fossil fuels in the form of coal, oil, and natural gas have powered the technology and transportation networks that drive society. This threatens the supply of energy and causes enormous strains to the environment. The international energy agency projects a 33% increase in oil consumption by 2020, which would affect the use and number of automobiles in the world affecting the environment, too. Besides, the atmospheric concentration of CO₂ has increased by 31% above pre-industrial levels because of the gas emissions resulted from the extensive use of fossil fuels in factories, automobiles, power plants and other waste vents. In addition, fossil fuel resources doesn't guarantee a sustainable future of energy which indicates even more the importance of finding alternative, sustainable, eco-friendly and cost-effective sources. For this purpose, this study was conducted to develop a promising technology and an effective solution that's ensured to be able to replace the fossil fuel resources in order to overcome the challenges of energy and environmental pollution all over the world. One such energy-saving technology is a fuel cell; it uses Hydrogen as the source of energy to produce electricity directly. The purpose of this study is to develop a more effective method for producing hydrogen fuel for the fuel cells in a more suitable way.

Keywords: Anaerobic digestion, H₂S & CO₂ removal, Steam Reforming, Water-gas Shift Reaction, Pressure Swing Adsorption.

Introduction

This study is conducted to provide a new solution for the problem of electricity in the world represented mainly in the full dependence on fossil fuel resources which causes a huge damage to the environment besides its increasing high cost and non-renew ability. The development of a new method for hydrogen production from methane steam reforming by the recovery of biogas using tri-ethanol amine absorption/stripping is the main purpose of the study. Hydrogen produced is then supplied to a PEM fuel cell to produce electricity.

Throughout the whole study, different types of publications have been used as resources like books, websites and popular media but mostly journals were the main reference. The number of resources and references was being ensured to be appropriate for the length of the paper.

Biogas purification by amines has been studied and conducted before many times on different samples of biogas but not for steam reforming. What's new in this study is that amines recovery of biogas is performed to supply methane to a steam reformer for hydrogen synthesis. Data about the requirements for the experiment were collected and analyzed to conduct a biogas purification by tri-ethanolamine.

After the methane is captured, it's supplied to a typical steam reformer for hydrogen production by reacting it with water vapor under 500 C to produce hydrogen and carbon monoxide which is then replaced by carbon dioxide and additional hydrogen in a water-gas shift reaction to produce 4 moles of hydrogen in total and one mole of carbon dioxide which is purified later in a pressure swing adsorption unit.

After pure hydrogen is extracted from the PSA, it's supplied to a fuel cell that typically produce hydrogen. An experiment has been conducted to measure the electric current generated by a typical fuel cell and the results were applied to the real scale project prototype.

Other studies showed some contrary points to the study's perspective in this paper. A journal by Shuji Fukahuri and his colleagues stated that methanol steam reforming produces more hydrogen-rich gases than methane steam reforming which is even harder to obtain. Our study, however, provides an alternative more economical way for obtaining methane and enhancing hydrogen production by methane steam reforming.

Final results and mathematical models for the project showed an apparent economical, scientific and environmental success. On the economical aspect, a business plan has been made to include the scope of the project, deliverables, objectives, success factors, cost analysis, risk management plan and cost control. On the scientific and environmental aspects, the project has been proved to have a positive impact on the environment and a proper scientific validity as will be shown. In conclusion, hydrogen synthesis by methane recovery of biogas and steam reforming provides the highest hydrogen production compared to previous studies. There have also been some defects and weak points that need to well-studied and improved. We are currently working on a new method of purification that uses less energy input and yields higher purification rate. Applications of the project are shown for how the project could be applied to real life and contribute in solving other problems.

Introduction & Hypothesis:

Relying on the fact that anaerobic digestion of manure produces, when decomposed by anaerobic bacteria, biogas that consists of 60% of methane, 40% of carbon dioxide and trace amounts of hydrogen sulfide, we claim that high amounts of hydrogen can be produced by harnessing the biogas yields of the process. The constituents of the biogas would then be purified to recover CH₄ and remove other hydrocarbons like CO₂ and hydrogen sulfide H₂S. When CH₄

is collected and reacted with water at a temperature of 500 C° it produces hydrogen and CO. Then, the products of that reaction would undergo another chemical reaction called Water-Gas Shift Reaction which gets rid of carbon monoxide and enhances hydrogen yields producing CO₂ as a byproduct. At last, hydrogen is recovered and CO₂ is removed in a PSA (Pressure Swing Adsorption) unit. At the end, the amount of hydrogen produced would be 4 moles of hydrogen for every mole of methane exceeding the traditional ways of hydrogen production which were only able to produce 3 moles of hydrogen at maximum.

Supposing that we use 500 tons of manure each day. Typically one ton of manure produces 800 m³ and we take 1/4 as a risk factor. Biogas produced by one ton would be 600m³/day . 600m³/day assigns to 396 kg methane which assigns to 24688 moles of methane and we take a risk factor of 1/5 which leaves us with 19750 moles. Having that each mole of methane produces 4 moles of hydrogen, then we should be getting 79000 moles of hydrogen which means 79 kg or 876 m³ hydrogen per one ton. 500 tons of manure, the hydrogen yield should 438000m³/day taking into account the risk factors.

Experiment:

Variables: These are the dependent and independent variables that affects our conducted experiments shown in Table (1):

Table 1: Variables affecting the conducted experiments

Experiment	Independent Variable		Dependent Variable	
	Variable	Method	Variable	Method
Anaerobic Digestion	Temperature	The process of anaerobic digestion of manure is conducted several time while changing the temperature each time. Temperature of the process is changed by changing the temperature of the water added to the system.	Amount of biogas produced	Amount of biogas produced should be changed according to the change in temperature of the system because temperature is as a matter of fact a factor that affects anaerobic bacteria.
		Temperature of the water is measured by a typical thermometer in units of Celsius.		The increase or decrease of the biogas produced is measured by exposing the gas to a flame and observing the intensity of burning.
	pH	pH of the system is also changed by changing the pH of the water added to the system each time.	Amount of biogas produced	Amount of biogas produced is expected to change because bacteria is affected by the system's pH.
		pH is measured by a typical pH meter.		Same method is used to measure the increase or decrease of production.
Fuel Cell Exp.	Amount of Hydrogen supplied	This experiment is conducted to measure the electric current produced by the fuel cell. A reaction is conducted between Sodium Hydroxide and Aluminum to yield hydrogen that's supplied to the cell. Amount of hydrogen produced is changed by changing the amounts of reactants each time.	Electric Current	Since the fuel cell uses hydrogen to produce electricity, then the amount of hydrogen supplied should be a factor that affects the electric current produced. Electric current is measured by a typical ammeter in units of Ampere

Other parts of the project that have been included in previous studies have some standard factors and variables that have a typical impact on the mechanism of these parts and how the processes work.

In Table (2) listed the variables and factors that affect each of these parts:

Table 2: Variables affecting different parts of the project plant

Procedure	Variable	How it affects the process
Biogas Purification By Ethanolamine	Concentration of ethanolamine	Higher concentration of Tri-ethanolamine guarantees higher purity and better recovery of CH ₄ ; the higher the concentration of the absorbent, the more carbon dioxide and hydrogen sulfide removed.
	Temperature	The absorption needs to occur under temperature of about 20 to 40 C. So any change of temperature could result in a less efficient absorption.
	Pressure	Increasing the pressure leads to an increase in the solubility of the absorbed gases which consequently enhances the efficiency of the process.
Steam Reforming	Temperature	Methane steam reforming is highly effective under more elevated temperature. At minimum, the

of Methane		temperature should be 400-500 C° but increasing the temperature would give more desirable results.
	Pressure	Lowering the pressure has a positive impact on the process. Typically, The reaction performs preferably at lower pressure.
	Catalyst	The type of catalyst also influences the reaction. The better the catalyst preparation, the faster and more efficient the reaction performance. Ni-based catalysts have showed the best results when compared to other Rh-based, Ru-based and Pt-based catalysts.
	Industrial materials	Materials used for construction of the container, heat exchangers, and combustion chambers are also responsible for the heat transfer and temperature control which affects the reaction mechanism. For example, materials used for heat exchangers should be good conductors of heat to ensure the proper temperature supplied to the reaction.
PSA (Pressure Swing Adsorption)	Adsorbent Material	The quality of the adsorbent beds used in the process contributes to how efficiently carbon dioxide is removed and how much hydrogen gas is recovered.
	Pressure	In the adsorption step of the cycle: the higher the pressure, the more successfully the adsorption goes. However, in the regeneration step: lowering the pressure leads to better and faster regeneration.

Constants & Control: To conduct our experiments correctly we had to keep some factors unchanged. This is a list of the constants in each experiment;

Anaerobic Digestion:

- Oxygen concentration is kept zero in all trials for the bacteria to work.
- Temperature is kept constant when testing the effect of pH on the process. Temperature is normalized (raised or decreased) by the addition of new water with a certain temperature.
- pH is kept constant when testing the effect of temperature on the process. pH is kept constant by adding a buffer solution to the water to resist any change in pH during the process.
- Amount of manure used is kept constant in each trial.
- Amount of water added to the system is kept constant for all trials.

Fuel Cell Experiment: The type of the fuel cell is the same during all trials.

Materials & Methods: Mentioned are the materials used in each experiment conducted:

Anaerobic Digestion

- Three containers of the same size filled with 2 kg of cow manure each.
- Three 1-litre bottles of water with temperatures 35 C, 70 C and 100 C respectively.
- Three 1-litre bottles of water with pH 5.5, 6.5 and 7.5 respectively.
- Typical thermometer for measuring temperature.

Fuel Cell

- Three samples of aqueous NaOH with concentrations 1.5 M, 1 M, and .5 M respectively.
- Three sets of aluminum sheets of masses 10 grams, 7 grams and 5 grams respectively.
- Cylindrical beaker and pipes for the reaction system.
- Fuel cell circuit.
- Ammeter.
- Safety equipment.

Methods for prototype design

Listed here is a design plan including materials that are used to construct a prototype for the project. The plan is designed in a way suitable for a large scale plant. Each part has its specified design parameters and materials used to build it.

Anaerobic digestion:

- Cylindrical container made of steel-36 alloy (alloy of iron with minimum 20% chromium/nickel/titanium/copper/carbon) with a radius of 8 inches and a height of 12 inches.
- Outlet pipe made of the same alloy with a radius of 1 inch and a length of 3 inches.

Biogas Upgrading:

- Cylindrical container made of steel-36 alloy with a radius of 11.5 inches and a height of 19.35 inches.
- Outlet pipe with the same parameters as the previous one.
- Regulator on a distance of 1 inch from the biogas upgrader to regulate the flow of gases.
- Tri-ethanolamine solution.

Steam Reformer and Water-gas shift:

- Cylindrical containers made of the following alloy: (68% Ni, 8 to 32% Cr, with the balance consisting of iron and up to 2.5% Si and 2.0% Mn) to resist high temperature for long hours. The radius of each container is 14.5 inches with a height of 19.35 inches. Same outlet pipes are designed.
- A cylindrical container with dimensions that fit inside the steam reforming container (combustion chamber) made of steel-36 alloy and heat exchanger of length 5.35 inches made of copper to work as a good conductor of heat.
- Two cylindrical vessels for vapor generating on the outlet pipe of each WGSR container to provide water vapor for steam reforming.

PSA (Pressure Swing Adsorption):

PSA unit consists of a container made of the same alloy as steam reformers and water-gas shifters with the same dimensions.

- Adsorbent bed made of activated carbon.

PEM Fuel Cell

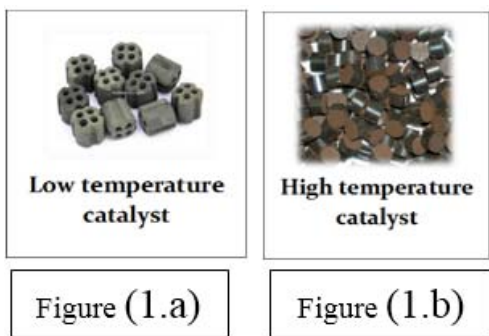
- A PEM fuel cell is used to generate electricity using hydrogen supply.

Catalysts Used

For steam reforming: Ce-ZrO₂ supported with 10 wt% Ni catalyst.

For high temperature water-gas shift: (Figure 1.b) Fe/Cu/Cr based catalyst with 8-12% Cr₂O₃ and 2% CuO. The catalyst is used in the form of pellets with a surface area of 30-100m²/g.

For low temperature water-gas shift: (Figure 1.a) Zn/Cu/Al based catalysts that have the following typical composition: 32-33 wt. % CuO / 34-53 wt. % ZnO, and 15-33 wt. % Al₂O₃



Data and Analysis:
Anaerobic digestion:

In this process anaerobic bacteria decomposes organic matter in the absence of oxygen to release biogas which is a mixture of several gases shown in Table (3). Results show that the biogas produced increased at a temperature of 35 C, was normal at 70 C, and decreased at 100 C as shown in Figure (2). When pH was 6.5 or 7.5, biogas production was at maximum, however, it was at minimum when pH was 5.5 as shown in figure (3).

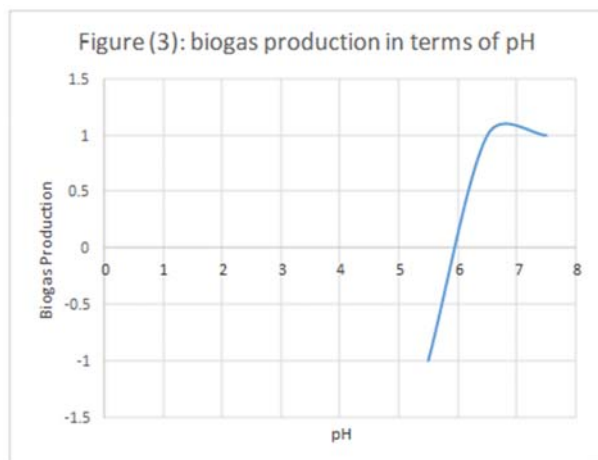
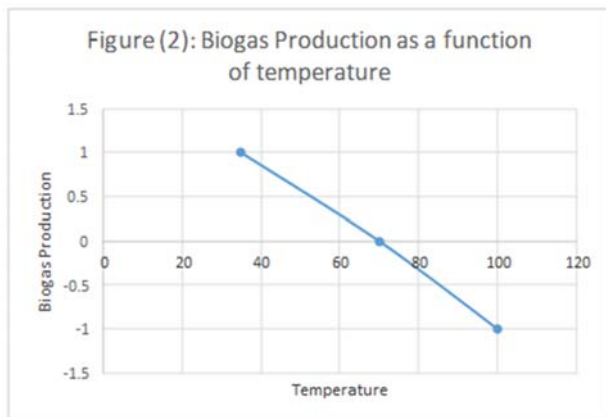
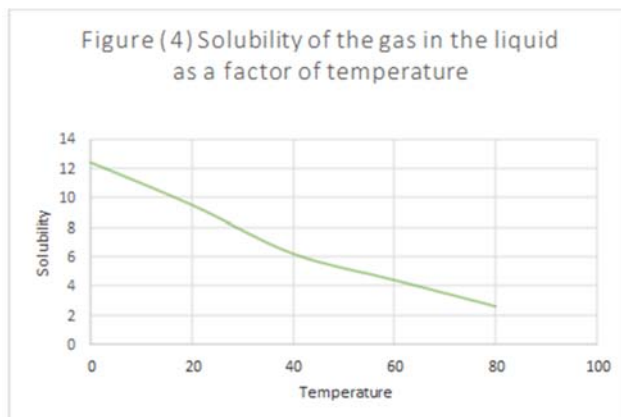


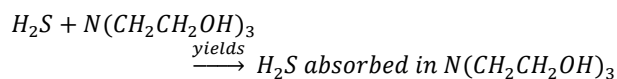
Table 3: Constituents of Bio-gas emitted from anaerobic digestion

Constituent	CH ₄	CO ₂	H ₂ S	NH ₃
Amount	60-75%	25-40%	100– 900 mg/m ³	—

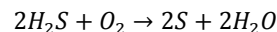
Biogas Upgrading: CO₂ and H₂S are removed from the stream using absorption by tri-ethanolamine solution. The temperature needed for the gas to be soluble in the liquid has to be low (between 20 °C and 40 °C), shown in Figure (4).



H₂S absorption: H₂S is absorbed by tri-ethanolamine in the following reaction:



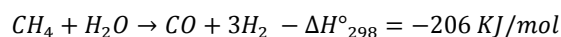
Then the products of this absorption are heated externally to regenerate tri-ethanolamine for reuse. The H₂S resulted from the regeneration is then reacted with oxygen to produce Sulfur (which is sold for high prices) and Water (which is recycled for reuse in the regeneration of tri-ethanolamine).



CO₂ absorption: tri-ethanolamine absorbs carbon dioxide in the same manner and then regenerated again by heating for reuse and the resulted carbon dioxide is used as a fuel for combustion chambers in the steam reformer to provide heat.

Steam Reforming:

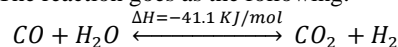
The methane reacts with water vapor under temperature of > 500 °C in the following reaction:



Rate of methane conversion varies with the amount of heat provided to the system as shown in Figure (5).The reaction occurs in a tubular reactor where the heat is provided by the burning of hydrocarbons inside a combustion chamber and heat transfer by heat exchangers.

Water-gas Shift Reaction:

This reaction is responsible for reducing the CO concentrations and increasing the amount of hydrogen produced. The reaction goes as the following:



The reaction goes in two steps as shown in Figure (6.a) and Figure (6.b) (Smirniotis, P. (2014).):

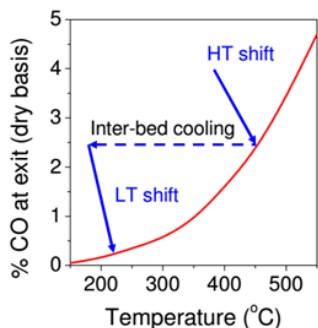


Figure (6.a): WGSR high and low temperature steps

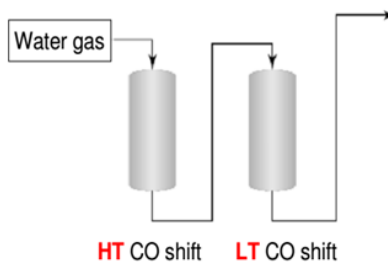


Figure (6.b): WGSR high and low temperature steps

Table 4: Comparison between high temperature and low temperature shifts

	Temperature	Catalyst	Pressure
High Temperature Shift	350 °C to 450 °C	Fe/Cr oxide based	10 to 60 bar
Low Temperature Shift	200 °C to 280 °C	Cu/Zn/Al oxide based	Less than 40 bar

PSA (Pressure Swing Adsorption):

This where the hydrogen is recovered and any other hydrocarbons like CO₂ and other contaminants are removed. The PSA used is a single layer adsorbent of activated carbon as shown in Figure (7): Pressure swing adsorption processes rely on the fact that under high pressure, gases tend to be adsorbed on solid surfaces. The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed.



Fig 7: PSA Activated Carbon Layer

The direct relationship between feed pressure and efficiency of the PSA is shown in Figure (8)

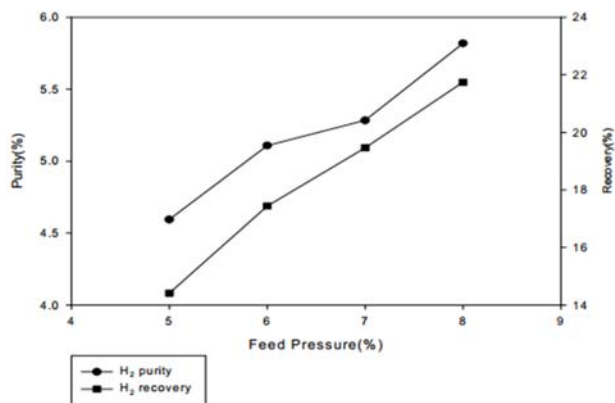


Fig 8: Purity of hydrogen as a function of feed pressure in PSA unit

At the end of this process, 4 moles of hydrogen are captured and supplied to a fuel cell to produce electricity.

PEM Fuel Cell: The process of generating electricity in the fuel cell goes as shown Figure (9) (Rayment, C., & Sherwin, S. (2003).):

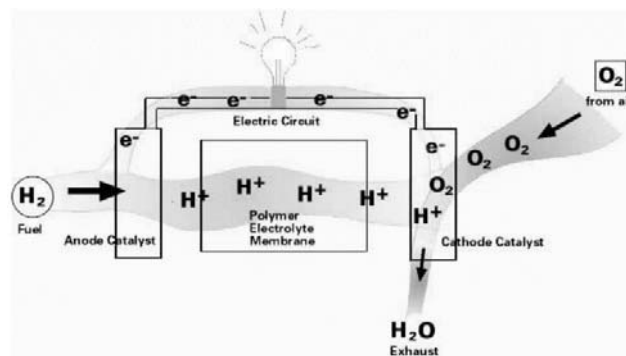


Fig 9: PEM fuel cell mechanism diagram

A modeled cost for a PEM fuel cell system based on projection to high volume manufacturing (Spendlow, J., & Marcinkoski, J. (2012).) is shown in Figure (10) below.

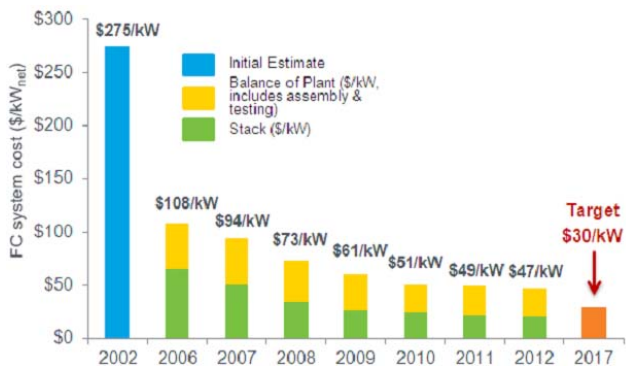


Fig 10: Modeled cost of a PEM fuel cell system based on projection to high volume manufacturing

To reach the target cost shown in Figure (10), we suggested using a special type of alloy as an alternative for the platinum catalyst. The alloy specifications are:

- Nano-scaled ratio of 85% platinum with 15% nickel as shown in Figure (11).

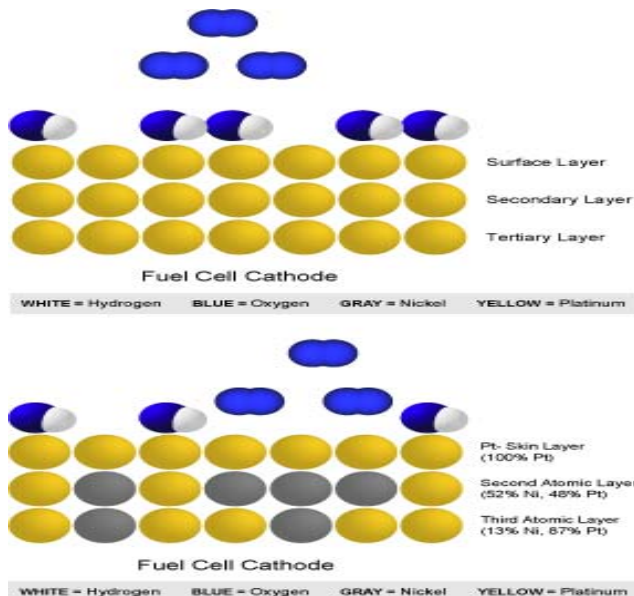


Fig 11: Platinum-nickel alloy structure

Discussion & Conclusions:

Based on the data collected and the experiment conducted, we were able to reach some conclusions about the project and compare them to other typical results and researches. Best biogas production was observed in the system with temperature 35 C and pH 6.5 and 7.5 which leads us to a conclusion that bacteria perform digestion under 3 constraints that have to be available in its environment:

- Constant temperature of about 35 C.
- An oxygen free medium.
- A pH from 6.6 to 7.6

The results were a lot similar to constraints stated in the Agricultural and Biological Engineering of Agricultural Sciences College paper of biogas production and reduction of odor from manure (Leggett, J., & E. Graves, R. (2014)).

CO₂ and H₂S are absorbed by tri-ethanolamine to recover CH₄ ready for steam reforming.

- Purity of the outlet methane gas is typically measured to have about 98.89% purity with a 95% recovery.

The effect of temperature on the steam reforming is measured to be directly proportional to performance quality of the reaction. Methane conversion is higher at higher temperature of about 600 and 700 °C.

The concentration of CO removed in each step of the WGS was:

- High Temperature Shift: goes from 45% to 4%
- Low Temperature catalyst: goes from 4% to less than 0.5%

The typical purity of hydrogen after the adsorption in PSA is 99.99%, while the typical recovery after the process is 87.91%.

In the PEM Fuel Cell, the alloy suggested is proved to reduce the cost of a PEM fuel cell by about 10% and increases its efficiency to about 98%. The alloy Pt₃Ni (111) showed the most significant improvements as shown in Figure (12).

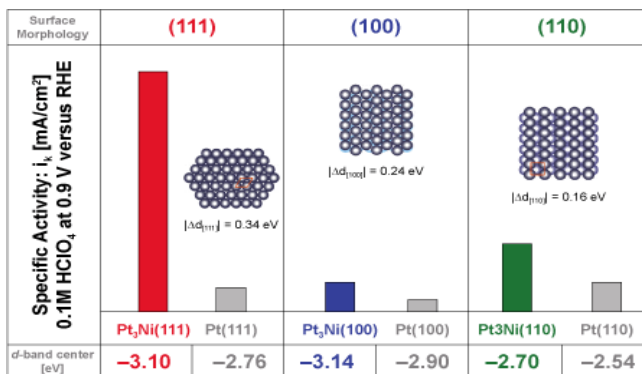


Fig 12: Pt₃Ni(111) catalysis efficiency

In conclusion, Hydrogen gas synthesis from biogas generated through anaerobic digestion by steam reforming has been investigated in this study. Based on the results of the study, 4 moles of hydrogen are to be generated for each mole of methane while other previous solutions and researches were only able to reach 3 moles of hydrogen. Also, harnessing the biogas yield from manure digestion protects the environment from the extreme danger of greenhouse gas emissions. Although the construction of the prototype needs a quite high cost, the economical aspect of the project is cost-effective compared to other hydrogen production methods. It can be concluded that the design requirements specified for the solution, which are efficiency, eco-friendly and cost-effectiveness, were clearly met by the methods used in the project compared to other solutions which indicates the ability of the solution to solve problems of energy and environment in the world.

The amount of hydrogen produced can be used in many industrial and life applications. Listed is some of the wide applications that use hydrogen as a main source of power:

Automotive and transportation equipment :

Many automobiles use hydrogen as fuel to provide power by a fuel cell. Such kinds of automobiles give off no harmful exhausts to the environment as shown in figure (13).

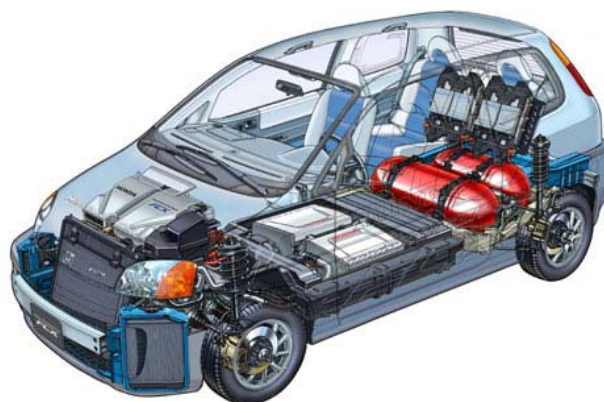


Fig 13: fuel cell applications in cars

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