Parametric Study of Palladium/Graphene Catalyst On-board Steam reformer for hydrogen generation from IC engine’s waste

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Abstract—Climate change is recognized as one of the greatest environmental threats facing the World today and it has long been appreciated by governments that reducing the impact of the IC engine powered motor vehicle has an important part to play in addressing this threat. This article presents the parametric study of a palladium (Pd)/ graphene oxide (GO) catalyst on-board hydrogen generator, which would have targeted function to make the vehicle energy efficient and improve the emission. The optimization of the concentration of GO and Pd has been conducted with COMSOL software. The gas chromatography analysis on exhaust of a 4-stroke spark ignition engine has been conducted and found that the concentration of exhaust is 0.5% H2, 0.5% CO, 11% CO2, 21% UHC and H2O. The Pd/GO catalyst hydrogen generator is expected to reformate the exhaust gas about 35% H2 (clean fuel), 5% CO, 10% CO2, 5% UHC, and H2O. The enriched and heat-treated 7% of hydrogen is considered to be pumped directly into the engine. It is expected that Pd/GO catalyst hydrogen generator would be able to save the engine fuel consumption about 12% for 1.4 -1.6 litre engine and reduce green house gas (GHG) emission about 40%.

Index Term—Pd/GO catalyst; Reformer; Hydrogen; Exhaust of IC engine; Green house gas

1. INTRODUCTION
Exhaust gas reforming is defined as the process, which provides hydrogen-rich reformate from exhaust gas purification treatment that contains a catalyst to promote the production of hydrogen and reduction of emissions. The author Abu Jrai (2008)[1] stated that exhaust gas reforming is an on-board hydrogen production method for IC engine and the combination of all the basic reforming processes which is located between the reformer and fuel cell. The largest part of most exhaust gases are nitrogen (N2), water vapour (H2O) and carbon dioxide (CO2). A relatively small part of combustion gas is toxı such as carbon monoxide (CO) from incomplete combustion, hydrocarbons from unburned fuel, nitrogen oxides (NOx) from excessive combustion temperatures, and particulate matter.

Currently the most developed and used technology for generation of hydrogen is the reforming of hydrocarbons. Hydrogen can be produced from a wide variety of feedstock available everywhere. As production technologies develop, hydrogen might prove to be the most present fuel available [2]. Studies on exhaust gas reforming found that high temperature exhaust gas (800–900 °C) can produce more than 30% of hydrogen in the reformed gas. However, for low temperature exhaust gas (500–700 °C), hydrogen production can be achieved up to only 20% of the reformed gas [3]. Palladium is a chemical element with symbol Pd and atomic number 46. Over half of the supply of palladium and its congeners platinum goes into catalytic converters, which convert up to 90% of harmful gases from automobile’s exhaust (hydrocarbons, carbon monoxide, and nitrogen dioxide) into less-harmful substances (nitrogen, carbon dioxide and water vapour) [4]. In the field of catalysis, palladium appears to be particularly important among the noble metals. Graphene is a single, tightly packed layer of carbon atoms that are bonded together in a hexagonal honeycomb lattice. Due to its extraordinary thermal, mechanical and electrical properties, graphene has aroused interest both for theoretical studies and applications [5]. Graphene has a unique structure which is the “thinnest material” in its free form. Graphene also have a good electronic properties, high thermal conductivity of 5000 Wm−1K−1, electric conductivity of 200000 cm−1, high surface area and excellent dispersion performance [6,7].

Catalysis is the hidden gem in environmental and chemical industries. While the use of catalysts is most commonly known in automotive catalytic converters, they are routinely used in other applications including gasoline, automobile lubrication and its additives, and the synthesis of fine chemicals. In addition to their economic impact, catalysts play a critical role in developing sustainable and environmentally friendly processes. The fifty highest-produced chemicals by volume in the US correlate with a substantial carbon footprint via the emission of carbon dioxide and other harmful gases into the earth’s atmosphere. Currently thirty of these processes have employed catalysts to reduce the emissions released and waste generated as investigated [8].

Despite catalysis emerging in the forefront of developing sustainable, efficient processes, industries still struggle to successfully develop such processes. The E-factor, one of the most straight-forward and useful green chemistry metrics, is defined as kilograms of waste produced per kilograms of product [9]. While catalysts have proven to assist in product selectivity, future advancements in process efficiency can be achieved by developing immobilized catalysts for use in continuous production methods. Over half of all chemicals
produced are still made using traditional batch reactions, yet continuous reactions offer unique advantages including intensified mixing, smaller volume to heating ratio, and safer operating conditions as found out [10]. The highly reproducible nature and therefore the robust application of continuous processes in the production of hydrogen from the exhaust of internal combustion engine has led to an increased interest in developing the proposed technology.

2. METHODOLOGY

2.1 Characteristics of Exhaust Reformer

Steam reformer reforms exhaust gas of internal combustion engine reducing the toxic emission products and increasing the engine efficiency. This device will convert exhaust gas into hydrogen, water and carbon dioxide and the fed the generated hydrogen back to IC engine. The IC engine exhaust gas and steam will pass through the Pd/GO catalyst onboard steam reformer and hydrogen will produce with chemical reaction as shown in Fig.1. The gas chromatography-mass spectrometry (GC-MS) has been used to characterize the percentage of gas at the outlet port of the reformer in terms of H₂, CO₂, CO, and NOx.

2.2 Exhaust Reformer

The steam reformer is the second phase of the development of the exhaust reformer. The catalyst is placed inside the reformer. The steam reformer is modeled by using ANSYS. Fig. 2 shows the graphene oxide (GO) and palladium catalyst based steam reformer. The full reformer is divided into three zone: upstream, middle and downstream. The upstream is called oxidation cell, which is connected with the engine exhaust manifold, the middle is the catalytic cells, and downstream is the gas splited zone which hydrogen splited port is connected with the engine intake manifold through heat exhanger to pump the hydrogen into the intake manifold of the engine. The heat exchanger exchanges heat to the surroundings through the coolant and allow for isothermal conditions, which allows for the assumption on single pressure and single temperature values to be used to characterize the
whole capacity state changes. Closed volume around the intake manifold to account for mass flow of conventional fuel, hydrogen, and air for the engine is used. The oxidation cell has steam and steam injection ports and uses to mix the exhaust gas and steam. The temperature of exhaust gases drops immediately with the mixture of the steam and forward to the catalyst cells.

When the desired temperature of 70–90°C is achieved, the produced hydrogen is stored in the tank for usage in the IC engine as an alternative fuel source to save fuel consumption. The amount of hydrogen supplied to the engine will be 7% of total Hydrocarbon fuel supply. The amount of hydrogen supplied to the engine is limited by the interior design of the engine. It is recommended to supply maximum amount 7% of hydrogen with the hydrocarbon fuel, which will be controlled by using a crankshaft rpm sensor. Theoretically, the hydrogen production by the reformer will be increased if the engine operating rpm is 4000rpm and above. The supplied hydrogen temperature to the engine is expected to be 90°C. The main reason for this temperature is to make the fuel atomized and vaporized in the engine cylinder, which will help the engine to achieve 95% fuel combustion (Rahman et al., 2015). In the conventional engine, the amount of fuel combustion in the engine is about 80-90%. Thus, this innovative technology
would be able to save fuel about (7%+5%=12%) or 12% and
reduce the GHG emission about 35%.

2.3 Synthesizing of Pd/GO
Synthesizing the characteristics of Pd/GO has been developed experimentally [6] According to Hummers and Offeman method, \( \text{H}_2\text{SO}_4/\text{KMnO}_4 \) and the oxidation of graphite powder used to produce graphene oxide. The synthesizing is briefly adding graphite (2 g) into concentrated \( \text{H}_2\text{SO}_4 \) (50mL) in ice bath followed by \( \text{NaNO}_3 \) (1 g) and \( \text{KMnO}_4 \) (7 g) under continuous stirring. The suspension is then moved to the warmed bath at 35°C after 2 hours. The mixture is then poured into 5L flask ice bath and around 30% of \( \text{H}_2\text{O}_2 \) was added until no gas was longer detected. Next, the suspension was filtered and washed with 0.1 M \( \text{HCl} \) solution and distilled water and centrifuged at 3000 rpm. Finally, graphene oxide (product) was freeze-dried and stored in the vacuum desiccators until further use. Pd/G and PdO/GO is then was impregnated with some combination of \( \text{H}_2 \) and \( \text{O}_2 \) gases. GO (0.9 g) was mixed with 0.21 g of Pd(OAc)\(_2\) into 90 mL of distilled water. The result of dark yellow was dispersed for 5 minutes and stirred for 24 h to promote the intercalation of Pd\(^{2+}\) on the GO surface. Then, the product was the filtered and washed by distilled water few times before centrifuged at 3000 rpm and freeze-dried, yielding the dispersion of Pd\(^{2+}\) on GO (Pd\(^{2+}\)/GO)[2]. Other method for synthesizing graphene oxide-palladium is by sonicated graphene oxide (0.1 g) into deionized water until homogenous substance obtained. Then, added the palladium nitrate (210 μL) to the homogenous substrate and agitated by using a magnetic stir plate. Next, the substrate was then placed in microwave where 100 μL of hydrazine hydrate solution (25% in \( \text{H}_2\text{O} \)) was added into that mixture with full power (1000 W) for 60 seconds [11, 12,13]. Finally, black flakes appeared as graphene oxide-palladium.

Results from the impregnation method shows that both Pd/G and PdO/GO have excellent catalytic activities for carbon-carbon cross-coupling reactions with their good distribution of small Pd on graphene surface.

2.4 Mathematical Model
The wall velocity is set as zero and inlet velocity for heating tubes is set as 1m/s. The flow properties are defined by the following equation.

\[
L_{\text{entr}} \nabla \rho + \nabla \left( (\nabla \rho) \right) + \rho \rho \mu \frac{2}{3} \nabla (\rho \mu^2) = n p_{\text{entr}}
\]

Then the outlet flow properties are defined by the following equations;

\[
\nabla \rho + \left( (\nabla \rho) \right) + \rho \rho \mu \frac{2}{3} \nabla (\rho \mu^2) = p_0
\]

with \( p_0, \rho_0, \mu = 0 \)

According to Darcy’s Law, \( \rho (\mu) = Q_m \)

\[
\mu = -k \rho \nabla p_i
\]

The mass flow rate of air, hydrogen and exhaust gas can be estimated by using the equation

\[
\begin{align*}
\dot{m}_{\text{a},\mu} &= \frac{C_{d,\mu} A_{\mu} P_{\mu}}{\sqrt{R_{\mu} T_{\mu}}} \left( \frac{P_{\mu}}{P_a} \right)^{\frac{1}{\gamma_a}} \left( \frac{2 \gamma_a}{\gamma_a - 1} \left( 1 - \left( \frac{P_{\mu}}{P_a} \right)^{\frac{\gamma_a}{\gamma_a - 1}} \right) \right)^{\frac{1}{2}} \\
\dot{m}_{\text{H},\mu} &= \frac{C_{d,\mu} A_{\mu} P_{\mu}}{\sqrt{R_{\mu} T_{\mu}}} \left( \frac{P_{\mu}}{P_a} \right)^{\frac{1}{\gamma_a}} \left( \frac{2 \gamma_a}{\gamma_a - 1} \left( 1 - \left( \frac{P_{\mu}}{P_a} \right)^{\frac{\gamma_a}{\gamma_a - 1}} \right) \right)^{\frac{1}{2}} \\
\dot{m}_{\text{CO},\nu} &= \frac{C_{d,\nu} A_{\nu} P_{\nu}}{\sqrt{R_{\nu} T_{\nu}}} \left( \frac{P_{\nu}}{P_f} \right)^{\frac{1}{\gamma_f}} \left( \frac{2 \gamma_f}{\gamma_f - 1} \left( 1 - \left( \frac{P_{\nu}}{P_f} \right)^{\frac{\gamma_f}{\gamma_f - 1}} \right) \right)^{\frac{1}{2}}
\end{align*}
\]
where, \( C_{d, a} \), \( C_{d, h} \), and \( C_{d, f} \) are coefficient of discharge for air, hydrogen and gasoline, respectively. \( A_{v, a} \), \( A_{v, h} \), and \( A_{v, e} \) are restrictions flow area for air, hydrogen and exhaust gas, respectively. \( P_a \), \( P_h \), and \( P_e \) the air, hydrogen, and exhaust sources’ pressures, respectively. \( \gamma_a \), \( \gamma_h \), and \( \gamma_e \) are the air, hydrogen, and exhaust specific heat ratios, respectively. The mixture of exhaust gases and steam pass to the catalyst cells and form the chemical reaction as shown in Figure 3 and generate the hydrogen (H\(_2\)), carbon dioxide (CO\(_2\)) and \( m \) water (H\(_2\)O). 

The hydrogen pumps to the engine cylinder, CO\(_2\) uses to heat the product of reformer H\(_2\)O and recycled to the reformer. Therefore, the rate of mass change inside this capacity can be given by the continuity equation [14]:

\[
\frac{dm}{dt} = \dot{m} - \dot{m}
\]

(4)

with \( \dot{m}_o = \dot{m}_{CO_2} + \dot{m}_{H_2} + \dot{m}_{NO_x} + \dot{m}_{UHC} + \dot{m}_{Steam(H_2O)} \) and \( \dot{m}_i = \dot{m}_a + x\% . \dot{m}_{H_2(f)} + (1 - x\%) \dot{m}_{C(f)} \)

where, \( \dot{m}_m \) is the intake manifold mass content, \( \dot{m}_i \) is the input mass flow to the intake manifold, and \( \dot{m}_o \) is the outflow from engine cylinders, \( \dot{m}_{UHC} \) is the outflow of un-burn hydrocarbon, \( x\% \) is the percentage of H\(_2\) pumps to the engine cylinder, \( \dot{m}_{CO_2} \) is the mass rate of conventional fuel (gasoline). The mass-balance equations for the model are the Maxwell-Stefan diffusion and convection equations at steady state:

\[
\nabla \cdot \left( \rho \omega_i \mathbf{v}_i \right) + \sum_j (D_{ij} \nabla 
abla \cdot \left( \rho \omega_j \mathbf{v}_j \right) + \left( \rho \omega_j \mathbf{v}_j \right) \nabla \cdot \left( D_{ij} \nabla \right) + \sum_j \left( \rho \omega_j \mathbf{v}_j \right) \nabla \cdot \left( D_{ij} \nabla \right) + \frac{\partial}{\partial t} \left( \rho \omega_i \mathbf{v}_i \right) = \rho \nabla \cdot \left( \rho \omega_i \mathbf{v}_i \right) + \sum_j \left( \rho \omega_j \mathbf{v}_j \right) \nabla \cdot \left( D_{ij} \nabla \right) + \frac{\partial}{\partial t} \left( \rho \omega_i \mathbf{v}_i \right)
\]

(5)

where, \( \rho \) is the density, kg/m\(^3\), \( \omega_i \) the mass fraction of species \( i \), \( x_j \) the molar fraction of species \( j \), \( D_{ij} \) is the \( ij \) component of the multicomponent Fick diffusivity, m\(^2\)/s), \( D_{ij} \) the thermal diffusion coefficient, kg/(m\cdot s)), \( T \) is the temperature, K, and \( R_i \) the reaction rate kg/(m\(^3\)\cdot s)). The flow of heating gas in the tubes is described by the Navier-Stokes equations at steady-state:

\[
\nabla \cdot \left( \rho \mathbf{v}_i \right) + \sum_j \left( \rho \omega_j \mathbf{v}_j \right) \nabla \cdot \left( D_{ij} \nabla \right) + \frac{\partial}{\partial t} \left( \rho \mathbf{v}_i \right) = \nabla \cdot \left( \rho \nabla \right) + \sum_j \left( \rho \omega_j \mathbf{v}_j \right) \nabla \cdot \left( D_{ij} \nabla \right) + \frac{\partial}{\partial t} \left( \rho \mathbf{v}_i \right)
\]

(6)

where, \( \rho \) is the density kg/m\(^3\), \( \mathbf{v} \) the velocity, m/s, viscosity, kg/(m\cdot s), \( P \) the flow rate, kg/m\(^3\) and \( p \) the pressure of the mixture in the tubes, Pa. At the outlet, viscous stresses are ignored and the pressure is set to 1 atmosphere.

3. RESULT AND DISCUSSION
Investigation of thermal variation in mechanical applications is one of the most critical processes. As long as the engine is running, the temperature of the reformer will increase by the heat from the high temperature exhaust gas. Temperature exchange between the catalyst bed and exhaust gas of the exhaust reformer needs to be determined numerically. Temperature profile of the catalyst bed and heating pipes during the reforming of the exhaust gas has been investigated by COMSOL Multiphysics.

3.1 SIMULATION STUDY BY COMSOL
The simulation of the exhaust reformer has been conducted by using COMSOL software based on Darcy’s velocity, pressure and temperature at heating tubes and catalyst beds. The simulation of steam exhaust reformer to estimate hydrogen production is the main focus for this study. Research done by author Dixon et al., (2014)[15] pointed that the amount of hydrogen produced is about 29.5% by using auto-thermal reforming process with methane as main fuel source. However, with steam reforming process, the estimation of hydrogen produced is around 30–40%. The meshing of the domain and boundary from the simulation are customized. The first step is to put the mesh on point 3 and 4 with maximum element size 0.0002. Secondly, the edge of boundary 4 is meshed with extremely fine mesh. Remaining mesh is meshed by using free triangular. The result of meshing is shown in the Fig.4. For the range of step and termination time, we used 5 and 1300s. The initial step is started from 0.001s with un-scaled tolerance.
The flow of gases in the catalyst bed is simulated by the Darcy’s velocity magnitude. For the flow of gases in the catalyst bed, the flow started as 1 m/s as defined by the input and steadily increased along the reactor. At the reformer exit, the velocity of the gases is about 2 m/s. For the steam flow in heating tubes, the initial velocity is $2 \times 10^{-2}$ m/s at the very beginning of the tubes and decreased to $1.4 \times 10^{-2}$ m/s throughout the length of the heating tubes as shown in Fig. 5. The pressure at the inlet of the reformer is 75 Pa as defined by the input and it is found that the pressure dropped uniformly throughout the length of the catalyst bed. At 0.05m, the input pressure dropped to about 50 Pa as shown in Fig. 6. At 0.1m of catalyst bed, the pressure again dropped to about 30 Pa. However, the outlet pressure of the catalyst bed is close to 0.

Fig. 4. Meshing (a) insulated heating pipes (b) catalyst bed.
The surface temperature of the heating tubes begins with 700K at the inlet as defined by the input. From there it decreased slightly along the heating tubes and increased to about 740K just before the outlet of the heating tubes as shown in Fig.7(a). The surface temperature of catalyst bed at the inlet is 900K as defined by the parameter and that of insulated foam is about 800K. However, the temperature dropped drastically to almost 620 K at 0.05m of catalyst bed length as shown in Fig.7(b). This happened because the hydrogen formation reaction absorbed heat. However, due to the heating from the heating tubes, the temperature climbs back to 660K at the outlet of the reformer.
At the inlet of the catalyst bed, the surface density of reacting gases is 0.27 kg/m$^3$. As the chemical reaction occurred, the density increased to 0.29 kg/m$^3$ at 0.05m. After that point, the density decreased gradually throughout the reformer length until 0.19 kg/m$^3$. The mass fraction of gas species is shown in Fig. 8(a) – 8(f) for the different composition of palladium and graphene. By considering only Palladium as catalyst, mass fraction of hydrogen is 0.1 and that of carbon dioxide is about 0.85 at the outlet as shown in Fig. 8(a). Although the mass fraction of methane is 0 at the outlet which indicates that all methane gases are consumed in this reaction, the mass fraction of water is 0.05. Therefore, there will be some steam left in the outlet products. Considering the Pd 70% and Graphene 30% as catalyst, the mass fraction of H$_2$ increased to almost 0.13 as shown in Fig. 8(b). This might be the effect of graphene in the catalyst. Also in this case, all the methane are consumed throughout the length of the catalyst bed. Figs. 8(f) shows the conversion of each species along the entire length of reformed catalyst. As the exhaust gas travels further along the catalyst bed, the deposition of hydrogen is increased because of faster reaction rate. In the plot for mass fractions, it can be seen that the entire reactor length is active in converting methane. Hydrogen concentration increased as the species goes into the entire reactor. However, the deposited mass fraction of hydrogen is less compared to CO$_2$ and H$_2$O due to the molecular mass of each species.

Temperature distribution by the energy exchange between heating pipes and reformed catalyst is investigated at 900 K
and 1100 K. It is studied that the steam enters the heating pipes at 900 K and exit at 632 K roughly. However, the exhaust gas enters at 900 K reaching minimum temperature first and eventually exits at average temperature of 680 K. For the 1100K, it can be seen (Fig.8(f)) that the mass fraction of hydrogen increases with increasing the reformer heating pipes length, while the other decreases with increasing the length of the reformer.
4. CONCLUSIONS

The proposed exhaust reformer with GO/Pd catalyst can promote the production of hydrogen from the raw exhaust gas of automobiles by steam reforming. The proposed principle of the exhaust reforming process can utilize the hydrogen as alternative fuel for IC engines, thus improving the fuel consumption, exhaust emissions and efficiency of the engine.

- GO/Pd steam exhaust reformer can promote 30.02% of hydrogen deposition at 900K exhaust temperature and 32.95% of hydrogen deposition at 1100K exhaust temperature. Therefore, the catalyst can promote more hydrogen deposition with higher temperature exhaust gas.
- The temperature distribution of the catalyst bed is in the range of reasonable working temperature between 1100K and 680K.

For future works, prototype of the GO/Pd exhaust reformer needs to be developed to investigate the accurate amount of hydrogen production by the reformer from the exhaust, emission reduction and fuel saving in experimentally. In summary, steam reforming process along with new GO/Pd catalyst can improve the production of hydrogen from exhaust gas of automobiles compared to other catalysts and reforming processes.

REFERENCES


AUTHOR PROFILE

Prof. Dr. Md. Ataur Rahman, obtained the Degree of Doctor of Philosophy in Engineering (Automotive Engineering) from the University Putra Malaysia (UPM) in 2005. He was appointed as a Visiting Fellow for “Designing Automation System for Off-road Vehicle” at the Mechanical Engineering Laboratory, The University of Tokyo, Japan for 2005-2006. He was appointed as an Assistant Professor at the Department of Mechanical Engineering, International Islamic University Malaysia (IIUM) in 2006. Later he was promoted by IIUM for the post of Associate Professor in 2010 and Professor in 2014. He was appointed as Team Leader of the “IIUM Smart Mobility” by the Department of Mechanical Engineering of IIUM for Proton Green Mobility Challenge (PGMC) 2012 on “Designing Electric Vehicle” and competed with the top 10 Universities in Malaysia. His team got the Overall Championship Award and 1st position for the both of “Fastest and Farthest Distance Travelling”. He is the Chairmen of IIUM Centre for Excellence of Electric Mobility. He is the author of two textbooks and number of book chapters. He has published 160 journal articles from his research works. He is inventor of five (5) patents on his research products including “electromagnetic actuator for the CVT system of passenger car, Evaporative thermal management system for EV battery” and etc. His interested research areas are the development of electric and hybrid vehicle’s systems including evaporative battery thermal management system, electronic power train, and electromagnetic 2-speed gearbox; intelligent system for swamp vehicle mobility; Off-road vehicle for peat terrain, renewable energy and automotive waste energy harvesting.