

HYDROGEN PRODUCTION FROM THE STEAM REFORMING OF PHENOL-  
PET SOLUTION USING NICKLE-PALLADIUM SUPPORTED CATALYST

BAHADOR NABGAN

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School of Chemical and Energy Engineering  
Faculty of Engineering  
Universiti Teknologi Malaysia

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To my beloved parents and brothers

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## ABSTRACT

As a sustainable and renewable energy carrier, hydrogen is considered as a key future fuel to make the low carbon energy schemes present. In recent years attention has been given for conversion of waste materials, including plastics towards production of hydrogen. Studies in this field are important because it resolves numerous problems brought about by plastic waste. Polyethylene terephthalate (PET) is one of the major products of plastic waste which constitutes a major threat to the environmental conservation efforts and living organism. Phenol has been chosen in this study as a solvent for PET toward hydrogen production since phenols are unwanted liquid by product of bio-oil from the biomass pyrolysis process. This study is to investigate catalytic steam reforming of phenol with dissolved PET over bimetallic nickel-palladium (Ni-Pd) supported on  $\gamma$ -aluminium oxide ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), zirconium oxide (ZrO<sub>2</sub>) and zeolite (ZSM-5) for hydrogen production. The scope of this research was based on the catalyst characterization, catalyst testing, process parametric study and reaction mechanism. The PET dissolution was screened in various solvents, and it was found that phenol is the most suitable solvent for this study. The catalytic steam reforming was carried out on the PET-phenol solution using a fixed bed reactor at atmospheric pressure. Developing a highly active and stable catalyst for hydrogen production from the steam reforming of waste products was the aim of this study. Supported Ni/Pd was prepared by impregnation method and screened on the steam reforming process. Ni-Pd/Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> was found to be the promising catalyst, as it was able to obtain as high as 95.6% phenol conversion, 69.5% hydrogen selectivity and remarkable performance even after 36 h. An in depth study of Ni-Pd/Al<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> catalyst was carried out from catalytic screening. Phenol concentration of 10 wt. %, temperature as low as 800 °C and total feed flow rate of 0.4 ml/min resulted in the highest hydrogen selectivity and highest PET-phenol conversion. Analysis on products composition indicated that steam reforming of PET-phenol generally produced aliphatic, high amount of aromatic compounds, together with moderate amount of cyclic compounds. The reaction conditions also led to alkylation of phenol by the reforming products from PET-phenol solution in the presence of the catalyst. Based on the product formation in the proposed reaction mechanism, free radical and carbenium ion mechanisms are of high chance to occur. In the parametric study five factors considered were temperature, feed flow rate of phenol+PET+water, N<sub>2</sub> flow rate, phenol concentration, as well as concentration of PET solution, while the responses were phenol conversion (Y<sub>1</sub>) and hydrogen selectivity (Y<sub>2</sub>). The result from the parametric study indicated that all the main independent variables have a significant influence on the dependent variable of Y<sub>1</sub> and Y<sub>2</sub> with the range of 47.2-97.6% and 49-71%, respectively. The most effective parameters in this study were temperature of 800 °C and PET concentration of 7 wt. %. In conclusion, this study explored new thought toward useful product from waste plastic materials. It provides a promising clean technology, which employed PET waste and phenol in the catalytic steam reforming toward production of hydrogen.

## ABSTRAK

Sebagai pembawa tenaga mampan dan boleh diperbaharui, hidrogen dianggap sebagai bahan bakar utama pada masa hadapan bagi menjayakan skim tenaga karbon rendah. Sejak beberapa dekad yang lalu, tumpuan terhadap penukaran bahan buangan, termasuk plastik untuk menghasilkan hidrogen telah diberi perhatian. Kajian dalam bidang ini adalah penting kerana ia dapat menyelesaikan banyak masalah yang terhasil daripada sisa plastik. Polietilena tereftalat (PET) adalah salah satu daripada produk utama sisa plastik yang merupakan ancaman utama kepada usaha pemuliharaan alam sekitar dan organisma hidup. Fenol telah dipilih dalam kajian ini sebagai pelarut PET untuk menghasilkan hidrogen disebabkan ia adalah produk cecair sampingan yang tidak diingini dalam bio-minyak hasil proses pirolisis biojisim. Kajian ini bertujuan untuk mengkaji pembentukan semula wap bermangkin di antara fenol dengan larutan PET ke atas dwilogam nikel-paladium (Ni-Pd) yang disokong pada  $\gamma$ -aluminium oxide ( $\gamma$ - $\text{Al}_2\text{O}_3$ ), lanthanum oxide ( $\text{La}_2\text{O}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ) dan zeolite (ZSM-5) untuk penghasilan hidrogen. Skop kajian ini adalah berdasarkan pencirian mangkin, ujian mangkin, proses kajian parametrik dan tindak balas mekanisme. Pelarutan PET dikaji di dalam pelbagai pelarut dan didapati bahawa fenol adalah pelarut yang paling sesuai untuk kajian ini. Pembentukan semula wap pemangkin dilakukan pada larutan PET-fenol dengan menggunakan reaktor turus tetap pada tekanan atmosfera. Pembentukan mangkin yang aktif dan stabil bagi penghasilan hidrogen daripada pembentukan semula wap produk buangan merupakan matlamat kajian ini. Ni/Pd yang disokong pada penyokong disediakan melalui kaedah impregnasi dan disaring dalam proses pembentukan semula wap. Ni-Pd/ $\text{Al}_2\text{O}_3$ - $\text{La}_2\text{O}_3$  didapati sebagai mangkin yang paling berpotensi kerana ia mampu mencapai 95.6% penukaran fenol, 69.5% kememilihan hidrogen dan mampu bertahan walaupun selepas 36 jam. Satu kajian yang mendalam terhadap parameter proses pemangkin Ni-Pd/ $\text{Al}_2\text{O}_3$ - $\text{La}_2\text{O}_3$  telah dilaksanakan. Kepekatan fenol 10%, berat suhu serendah 800 °C dan kadar aliran suapan cecair sederhana 0.4 ml/min menghasilkan kememilihan hidrogen dan penukaran PET-fenol yang tertinggi. Analisa terhadap komposisi produk menunjukkan bahawa pembentukan semula wap PET-fenol umumnya menghasilkan alifatik, sebatian aromatik yang tinggi, dan sebatian siklik yang sederhana. Keadaan tindak balas juga menyebabkan alkilasi fenol oleh pembentukan semula produk dari larutan PET-fenol dengan kehadiran mangkin. Berdasarkan pembentukan produk didalam cadangan tindakbalas mekanisme radikal bebas dan ion karbenium adalah yang paling berkemungkinan berlaku. Dalam kajian parametrik, lima faktor yang dipertimbangkan ialah suhu, kadar aliran suapan fenol+PET+air, kadar alir jisim (ml/min) nitrogen, kepekatan fenol, dan kepekatan larutan PET, sementara sandaran adalah penukaran fenol ( $Y_1$ ) dan kememilihan hidrogen ( $Y_2$ ). Hasil daripada kajian parametrik menunjukkan bahawa semua pembolehubah bebas utama mempunyai pengaruh yang penting terhadap pembolehubah bersandar,  $Y_1$  dan  $Y_2$ , dengan julat masing-masing 47.2-97.6% dan 49-71%. Parameter yang paling berkesan adalah pada suhu 800 °C dan kepekatan 7 % berat PET. Sebagai kesimpulan, kajian ini meneroka peluang baru untuk produk yang berguna daripada bahan buangan plastik. Ia menyediakan teknologi bersih, menggunakan sisa PET dan fenol bagi pembentukan semula wap bermangkin untuk penghasilan hidrogen.

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**LIST OF ABBREVIATIONS**

S/C	–	Steam to carbon ratio
FPS	–	Fuel processing system
ATR	–	Auto thermal reforming
O <sub>2</sub> /C	–	Oxygen to Carbon ratio
TCD	–	Thermal conductivity detectors
FID	–	Flame ionization detectors
SEM	–	Scanning electron microscopy
TPR	–	Temperature-programmed reduction
TPD	–	Temperature-programmed desorption
TPO	–	Temperature-programmed oxidation
XRD	–	X-ray diffraction
HPLC	–	High performance liquid chromatography
WGS	–	Water gas shift reaction
BET	–	Brunauer, Emmett and Teller
OSC	–	Oxygen storage capacity
TOS	–	Time on stream
LH	–	Langmuir–Hinshelwood
ER	–	Eley–Rideal
RDS	–	Rate-determining step
EPA	–	Environmental protection agency

**LIST OF SYMBOLS**

$^{\circ}\text{C}$	–	Degree celsius
K	–	Kelvin
g	–	Gram
mL/min	–	Milliliter per minute
$C_A$	–	Concentration of phenol
$C_B$	–	Concentration of water
a	–	Reaction order with respect to phenol
b	–	Reaction order with respect to water
$k_{\text{rxn}}$	–	Kinetic constant of reaction
$k_{A(p)}$	–	Kinetic constant corresponding to phenol
$k_{B(w)}$	–	Kinetic constant corresponding to water
$R^2$	–	Coefficient of determination
$r_{\text{ph}}$	–	Reaction rate
$E_a$	–	Activation energy
R	–	Gas constant
$Q_{\text{ph}}$	–	Phenol flow rate
mmol	–	Millimole
$\mu\text{mol}$	–	Micromole
$W_{\text{cat}}$	–	Catalyst weight
$X_{\text{ph}}$	–	Phenol conversion
J	–	Joule
Wt. %	–	Weight percent



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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of Study**

Depleting fossil fuels and environmental concerns has motivated the research for production of clean renewable fuel. As an ideal candidate for a clean and sustainable energy source, hydrogen has attracted notable research interest in recent years. Hydrogen has excellent safety record and can be transported, stored and used just as other numerous fuels [1]. In recent times, hydrogen is produced from sources such as water, coal gasification, acetic acid, natural gas, butanol, ethanol, methane, glycerol, bio-oil and naphtha catalytic steam reforming [2]. Not only has the development of hydrogen production as a renewable fuel been a keen area of research, attention has also been given to conversion of waste materials to energy, including plastics [3, 4]. Studies in this field are of great importance because it resolves numerous problems brought about by plastic waste together with other forms of waste, especially after their consumption.

Among different types of plastic, Polyethylene terephthalate (PET) is one of the main sources of packing materials such as bottles for mineral water and soft drinks all around the world. A major uniqueness of PET is its wide application as packaging material, especially in food industry. This is mainly due to its non-hazardous nature to health as well as other living organisms. Even though it has no direct hazardous impact to environment, its percentage in the waste stream coupled to its low degradation makes it harmful [5]. One of the chemical methods used to recycle PET, is solvolysis, such as methoanalysis and glycolysis [6]. With the great

advantage that a portion of PET can be recycled straight to virgin PET [7], or to raw constituents [8] via chemical alteration techniques (such as glycolysis and hydrolysis), yet the main problem of recycling PET is that a considerably big amount returns to waste dumps. Consequently, any novel implementation or artificial use of waste PET would be a momentous relief to the surroundings [9] and this is one of the main emphasis of the current study. Therefore, generation of hydrogen from plastics is indeed a promising technology environmentally and economically [10].

Base on the realities that majority of the polymers dissolve into hydrocarbon combinations, co-processing unwanted polymers as part of the feed to standing processing plants, both thermal and catalytic, is a considerable attitude for the third reprocessing polymers. Since they are actually hydrocarbons of high molecular weight and that those methods are completely proven, they would not need significant practical amendment [11, 12]. The method that had been investigated in place of an explanation concerning plastic recycling is so-called dissolution/precipitation (DR). This method for energy recovery has several advantages over approaches similar to waste incineration and pyrolysis [13]. PET is considered as a momentous portion of the curbside mixture and indicates a significant recycling prospect [14].

However, as most studies in the polymer recycling process were carried out in batch reactors, there are some difficulties to apply the process such as continuous mode in polymer recycling industry. In order to achieve such development, polymer reforming has to be carried out in continuous process mode. Nonetheless, polymer waste in its solid waste is difficult to be fed into reactor continuously. Thus, there is a need to develop a method that enables smooth continuous feeding of polymer waste into the reactor, as there are many advantages associated with this process. Studies by previous researchers [15, 16] may serves as a possible solution to the mentioned problem. In their studies, the polymer is dissolved in compatible solvents to form solutions with reasonable viscosity. The polymer solution was then feed into the reactor to produce useful gas and liquid products using cracking/reforming process. However, such processes are very scarce in literature, and only limited to

small scale. Hence, it is necessary to investigate on catalytic reforming of polymer in larger scale.

As regards to the processes, there are different processes for hydrogen production, namely: steam reforming (SR), coal gasification, auto-thermal reforming (ATR), dry reforming (DR), partial oxidation (POX), thermolysis, pyrolysis, and electrolysis, which show effective routes for hydrogen technology. Among these, steam reforming is the most studied route since it produces the highest hydrogen yield compared to other methods such as ATR, POX, and DR [17, 18].

In studies of catalytic steam reforming, phenol ( $C_6H_5OH$ ) is often used as a model compounds. As an important constituent in the aqueous portion of bio-oil, (lignin-derived) phenol constitutes about 38% by weight [19]. Since PET is soluble in phenol, it has been selected in this study as a feedstock [20] which can make unique product that contains two main waste component (phenol as a solvent and PET as a solute). The phenols and phenolic compounds are not considered as fuels and they are corrosive to combustion engines. It can also be produced from renewable sources, like biomass via fast pyrolysis procedure and more breakdown phenolics [21].

Steam reforming of phenol to produce hydrogen has been investigated over a wide variety of supported metal catalysts such as Ni, Rh, Fe, Rh-Fe, CaO, Pt, Pd, and Rh [22-25]. Meanwhile, numerous studies have shown that support such as  $\gamma$ - $Al_2O_3$ ,  $La_2O_3$ ,  $ZrO_2$ , MgO, and  $CeO_2$  also plays a critical role in the catalytic performance for hydrogen production from phenol steam reforming [22, 25, 26]. Matas Güell et al. found that Ni/K- $La_2O_3$ - $ZrO_2$  and Ni/ $CeO_2$ - $ZrO_2$  catalysts exhibited high activity in hydrogen production and good stability in phenol conversion [22]. However, the catalysts suffered in deactivation due to coke formation. Garbarino et al. studied ethanol and phenol steam reforming over Ni- $La/Al_2O_3$  catalyst under temperatures between 500 and 750 °C, GHSV = 54000  $h^{-1}$  of a gaseous mixture with the following composition: 39.3% He, 54.6% water, 4.1% ethanol and 2% phenol [27]. Operating at 750 °C  $H_2$  yield was achieved with 82% and phenol conversion of 88%.

Among the catalysts, alumina ( $\text{Al}_2\text{O}_3$ ) is the most commonly employed support in various thermal processes because of chemical and mechanical stability, low cost and high surface area for metal dispersion [28, 29]. The  $\text{La}_2\text{O}_3$  and  $\text{ZrO}_2$  as support materials have displayed a great vital catalyst-support interaction [30]. Bimetallic catalysts such as nickel on  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{La}_2\text{O}_3$  have been used for steam reforming [31] which are able to suppress the formation of coke. In addition to  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  has displayed prolong ability as reported by many researchers [32-34]. Among the different metals, although noble metals have higher activity and stability, their high cost advises the use of catalysts with transition metals. Ni is one of the most used metal in steam reforming processes due to its lower cost and excessive available in nature as compared to other noble metals [35]. Nevertheless, it is commendable that noble metals such as Rhodium (Rh), Palladium (Pd), Ruthenium (Ru), etc. are resistant to coke formation even at high temperatures ( $>700$  °C), thus provides prolong stability to catalyst [36-38]. It has been reported that co-loading of a small quantity of a noble metal to a non-noble metallic catalyst has significant effect on the overall catalytic activity and products selectivity [37, 39]. Recently, Pd-based catalysts have been widely investigated due to its lower cost and high performance in comparison to Pt-based catalysts. Lot of research efforts have been dedicated to it, such as formic acid oxidation on Pd and Pd-based catalysts [40, 41]. A two-step decomposition of metal organic compounds and successive reduction with  $\text{H}_2$  on magnesia powder to prepare Pd–Ni core-shell nanoparticles has been reported by Sao-Joao et al. [42].

In this study steam reforming of PET waste is the presented method that has designated for hydrogen generation. Based on prior studies, the literature to date on phenol steam reforming reaction is relatively limited and only a few studies have attempted to develop plastic recycling methods based on cracking reaction. In addition, no works has been issued on steam reforming of PET over supported Ni-Pd catalysts. In this study, a number of Ni-Pd catalyst supports, which are set by initial wetness impregnation technique, will be carried out.

## 1.2 Problem Statement

The disposal of plastic waste has caused numerous problems to the environment as it does not degrade. Many methods have been proposed including polymer catalytic cracking (pyrolysis), DR method [13] and the usage of biodegradable plastic to replace the conventional plastic. However, the energy consumption of cracking process is very high, and its use in liquid fuels production is hardly justified. In addition, most studies on catalytic cracking of polymer have been conducted in batch process, which is difficult to be applied in polymer recycling industry. There is a need to develop catalytic cracking of polymer in continuous mode [15, 16], since such process is more scalable and suitable for industry requirements. Nevertheless, development of catalytic cracking of polymer in continuous mode is challenging due to the lack of comprehensive studies. In order to develop such process, the compatible solvent for PET has to be determined, due to its limited solubility in many solvents. The production of bio-degradable plastic is also under debate due to the competition of the process with food production. Hence, it is proposed to combine the dissolution and catalytic reforming of polymer waste into the energy. There is no study done on this process yet according to the open literature, hence a detailed study on the process is needed. The main problem of PET molecule recycling is that it cannot be recycled to soft drink bottles again due to the smell and hygiene; thus, dissolution of PET into suitable solvent to produce energy in a new way is yet to be studied.

The high cost of catalyst is another major constrain to hydrogen production from phenol steam reforming process [23, 43-46]. Noble metals such as ruthenium, rhodium, palladium, iridium, platinum, and gold provide high hydrogen yield in the reforming reaction. However, the high cost of noble metals limited their further application. Accordingly, the search for non-noble metal catalysts with good activity and selectivity in the phenol steam reforming reaction would receive considerable attention. This will undoubtedly contribute towards making the process more economical, especially when reflected in terms of high and stable hydrogen production [47-49]. Nickel among non-precious transition metals shows good performances in steam reforming reaction.

Another problem is that phenol constitutes up to 38 wt.% of non-fuel product from pyrolysis of biomass in bio-oil production. Phenol is an attractive feedstock for hydrogen production as it is non-inflammable in nature and also water-soluble. Phenol is an unwanted, reactive and corrosive compound of pyrolysis oil and is not suitable for the internal combustion. Phenol also can be found in the industrial wastewater, for example from textiles and pharmaceuticals industry. Thus instead of producing carbon dioxide in the combustion or oxidation, converting phenol into hydrogen or employing phenol as a solvent for dissolving PET to generate new useful products can help to reduce greenhouse effect. Based on previous studies, no works on PET waste reforming over supported Ni + 1 wt.% Pd catalysts had been reported. In this study, several Ni-Pd catalyst supports, were carried out which may novel the study with improved catalyst as well as a new route towards hydrogen production.

### 1.3 Objective of Study

The detail objectives were divided into five, which are;

- a) to prepare and characterize the physical and chemical properties of the Ni and Pd supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and ZSM-5.
- b) to perform catalyst screening on the prepared catalyst in a fixed bed reactor for the PET-phenol steam reforming.
- c) to carry out an in-depth study of the promising catalyst on the catalytic steam reforming of PET-phenol solution towards hydrogen production, feed conversion and liquid product composition.
- d) to propose a reaction mechanism of the PET-phenol steam reforming in the presence of the catalyst, and
- e) to evaluate the significant and the interaction factors of the reaction parameter such as temperature, feed flow rate, mass flow, phenol concentration, as well as concentration of PET in phenol solution using design of experiment (DOE).

## 1.4 Scope of Study

The overall scopes of this work are divided into six according to the objectives, and methodology as listed below.

- a) 10 wt.% (Ni-Pd) on different type of supports,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and ZSM-5 were deposited using an impregnation method. The prepared catalysts were characterized by X-Ray Diffraction (XRD), the total surface area by BET, reducibility of Ni/Pd by temperature programmed reduction-hydrogen (TPR-H<sub>2</sub>), base properties by temperature programmed desorption-carbon dioxide (TPD- CO<sub>2</sub>), surface morphology and composition by SEM-EDX, and coke formation by thermogravimetry analysis (TGA).
- b) Prior to the preparation of PET-solvent solution, solvent screening was carried out using different pure solvents (phenol, methanol, hydrochloric acid, acetic acid, acetone, ethylene glycol, iso-octane, dimethyl benzyl amine, iso-propanol, dichloromethane, ethanol, xylene, toluene, benzene and sodium hydroxide) to determine the best solvent for dissolution of polyethylene terephthalate (PET). Phenol was the only solvent that easily dissolves PET at 90 °C. Functional molecules characterizations were also performed on PET by Fourier-transformed Infra-red (FTIR) spectrometry.
- c) The catalyst screening were performed at the temperature of 700 °C, 0.2 gram of catalyst, total feed flow rate of 0.4 ml/min (specifically (water:phenol:PET) ratio of (1:0.107:0.003)), 3 wt.% PET solution and 1-9 feed to steam ratio; in a fixed bed reactor operated atmospheric pressure. The liquid products were analyzed to obtain the conversion and product composition. In addition, the stability of each catalyst was evaluated in term on the conversion as of reaction time and rate of coke deposition. The PET-phenol solution sample was prepared from the dissolution of PET in pure phenol, the bottles of mineral water was cut in different size such as; 0.3, 0.5 and 1.0 cm<sup>2</sup>.
- d) An in-depth study in varying reaction parameters such as reaction temperature (600 to 800°C), amount of catalyst (0.1 to 0.3 g), feed flow rate (0.10 to 0.40 ml/min), concentration of phenol (10 to 30 wt.%), concentration



of PET solution (3 to 10 wt.%), mass flow rate (10 to 40 SCCM) was carried out for the optimal catalyst. Temperature programmed oxidation (TPO) and thermogravimetry analysis (TGA) analysis of coke for the used catalyst was also accomplished.

- e) Composition of the product was determined from scope (d) after performing catalytic reforming. The plausible mechanism was proposed for catalytic reforming of PET-phenol, based on the literature, compared to the composition of products, considering the effect of temperature and residence time.
- f) By using the selected catalyst, a parametric study was carried out on the catalytic steam reforming of PET solution in a fixed bed reactor. Two-level full factorial design was generated using Minitab® for this purpose. The factors studied were temperature (600-800 °C), total feed flow rate (0.1-0.4 ml/min), mass flow (10-40 SCCM), concentration of phenol (10-30 wt.%) and concentration of PET into solvent (3-7 wt.%), while the responses were feed conversion and hydrogen selectivity.

## 1.5 Significant of Research

In the literature, a few works discussed on recycling of PET via dissolution method and no study has been worked on catalytic steam reforming of PET toward production of useful energy. Whereas in this study, the performance of different supported Ni and Pd catalysts in PET reforming reactions were studied in details. Due to the numerous problems brought by the plastic waste, it is important to determine an effective method to handle them when disposed. Although extensive studies had been performed on catalytic cracking of plastic waste, it is still not ready to be adopted in the plastic waste recycling industry, due to many limitations that have not been solved yet. Some of the limitations include the storage and separation of plastic waste prior to the recycling process, process efficiency in term of energy consumption and waste conversion, and the difficulty to scale up the process into continuous process, due to clogging problem. Therefore, the new method, combining polymer dissolution and catalytic steam reforming in continuous process, is

suggested in this study as a solution towards plastic waste recycling. In addition, PET ascribed as the main packaging waste materials in the environment and since it contains high hydrogen content, it could be of great importance to use this plastic in order to handle an environmental concern towards value product of hydrogen. Palladium and nickel were the widest used transition metals for various steam reforming reactions, and both were suggested as appropriate materials because of their maximum catalytic performances. However, the detailed comparisons of Ni and Pd over M (M=  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and ZSM-5) catalysts in terms of catalytic behaviors in PET reforming reactions have not yet been officially published anywhere. Thus, catalytic behaviors of these different supported transition metals catalyst in steam reforming of PET-phenol solution are aimed in this study.

In addition to catalytic behaviors, the performance of hydrogen production from PET-phenol steam reforming reaction can be affected by many issues. Thus, it is important to use a method such as design of experiments (DOE) in order to decrease the number of experiments and to simplify the description of the significant operation conditions [50]. Moreover, in order to explain the products formation, as well as the effects of different parameters in catalytic reforming of polymers, proposing the possible reaction mechanisms could be significant as there was lack of research study in the literature. The study would benefit in a number of particular areas in terms of processing, such as a reduction of energy consumption and expenses of the catalyst, as well as the feed usage. The catalyst in this work (Ni with the addition of only 1% Pd) has a lower cost compared to the noble metal such as ruthenium (Ru), rhodium (Rh), platinum (Pt) and iridium (Ir). The study would be qualified to prepare a thought on reducing the catalyst to rise the hydrogen generation besides feed conversion. To the best of our knowledge, no study is reported in the open literature using a combination of polymer dissolution and catalytic cracking/reforming of PET to generate hydrogen, the result from this study is expected to expand the frontier of knowledge in the field of plastic waste recycling in the globe.

## 1.6 Thesis Outline

This thesis consists of five chapters. Chapter 1 states the research background, problems, research objectives, scopes and significance of research. Chapter 2 discusses the literature review including background knowledge on catalytic steam reforming of phenol, DOE, analysis techniques that are commonly used for characterization purpose in catalytic reforming, recent development for PET recycling and proposed reaction mechanism. Chapter 3 describes the experimental setup and the procedures followed during the research work which includes catalyst preparation, characterization methods on fresh and used catalyst, feed preparation, analysis of gas and liquid products, study on effects of reaction parameters towards process performances and products compositions as well as parametric study (DOE). Chapter 4 provides the data processing and discussions on the results, such as preparation and characterization of catalysts, preparation of feed for catalytic steam reforming reaction using dissolution technique and catalytic screening for performance and stability of the optimal catalyst, followed by proposed mechanism on catalytic reforming of dissolved PET into phenol as well as reducing the number of experiments using DOE. The conclusion from this research and the recommendations for future study is presented in chapter 5.

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