

HYDROGEN PRODUCTION FROM PHENOL STEAM REFORMING USING
NICKEL-COBALT MODIFIED TITANIA COUPLED MAGNESIUM
ALUMINATE NANOCOMPOSITE CATALYST

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This thesis is dedicated to my father, Muhammad Ali, and my mother, Amin Bano,
and teachers.

Special dedication to the memory of my late brother, Shaheed Zubair Abbas, whose
life was taken at a young age of 16 in a targeted terrorist attack in March 2012.
Though you are no longer with us, your memories and wisdom was pivotal to my
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ABSTRACT

Utilization of renewable and sustainable sources of energy has gained attention to replace conventional and non-renewable fossil fuels. Production of hydrogen by catalytic steam reforming of phenol (SRP) is anticipated to play a vital role to overcome energy demand in future. The objective of this study is to develop nickel (Ni) and cobalt oxide (Co_3O_4) supported titanium dioxide (TiO_2) and magnesium aluminate (MgAl_2O_4) nanocomposite for SRP towards selective hydrogen production. Hydrothermal method was used to synthesize TiO_2 microparticles (TMP), TiO_2 nanorods (TNR), spinel MgAl_2O_4 and Co_3O_4 nanocubes. However, wet impregnation method was used to synthesize MgAl_2O_4 -TNR and Ni/ Co_3O_4 promoted MgAl_2O_4 -TNR nanocomposite catalysts. The fresh and used catalyst samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, field emission scanning electron microscopy, Brunauer-Emmett-Teller with nitrogen, Fourier transform infrared spectroscopy and thermogravimetric analysis to understand the crystallinity, electronic state, surface morphology, pore structure, surface area and stability. Initially, a systematic thermodynamic analysis (TDA) was conducted to investigate the effect of various process parameters on output products composition. Optimal equilibrium reaction conditions according to TDA were found to be 550-750 °C reaction temperature, 1 atmospheric pressure and 5 wt.% phenol concentration. The catalytic activity test over Ni/TMP, Ni/TNR and Ni- Co_3O_4 /TNR was performed to investigate the role of Ni and Co_3O_4 on the effectiveness of different structures of TiO_2 support for SRP using a vertically aligned stainless steel tubular fixed bed reactor at 700 °C and steam to carbon ratio (S/C) of 15/1 at atmospheric pressure. After detailed screening, 10%Ni-5% Co_3O_4 /TNR catalyst showed phenol conversion of 92% and H_2 yield of 83.5%. However, addition of MgAl_2O_4 as co-support with TNR promoted by Ni/ Co_3O_4 was found very effective in phenol conversion with enhanced H_2 yield and prolonged stability. Using composite catalyst, 96.4% phenol conversion with ~70% H_2 selectivity and 88.6% H_2 yield were achieved. The operating parameters were investigated by statistical approach using response surface methodology (RSM) to obtain optimum responses in the form of phenol conversion and H_2 yield. Optimization of SRP by RSM revealed 92.5 % H_2 yield at optimal operating condition of 781.7 °C, 10.15 ml/h feed flow rate, 7.2 wt.% phenol concentration and 0.312 g of catalyst loading. The stability test showed composite catalyst continued its catalytic activity even after 400 h. Therefore, it can be concluded that MgAl_2O_4 -TNR promoted by Ni- Co_3O_4 catalyst has high prospective for application in steam reforming of phenol for selective and sustainable route for the production of hydrogen.

ABSTRAK

Penggunaan sumber tenaga yang boleh diperbaharui dan mampan telah mendapat perhatian bagi menggantikan bahan api fosil yang konvensional dan tidak boleh diperbaharui. Penghasilan hidrogen melalui stim pembentukan semula fenol bermangkin (SRP) dijangka dapat memainkan peranan penting dalam mengatasi permintaan sumber tenaga di masa hadapan. Objektif kajian ini adalah untuk menghasilkan nanokomposit nikel (Ni) dan kobalt oksida (Co_3O_4) yang disokong kepada titanium dioksida (TiO_2) dan magnesium aluminat (MgAl_2O_4) bagi SRP ke arah pengeluaran hidrogen yang selektif. Kaedah hidroterma telah digunakan bagi mensintesis mikropartikel TiO_2 (TMP), nanorod TiO_2 (TNR), spinel MgAl_2O_4 dan nanokub Co_3O_4 . Walaubagaimanapun, kaedah pengisitepuan basah telah digunakan untuk mensintesis mangkin-mangkin nanokomposit MgAl_2O_4 -TNR dan Ni/ Co_3O_4 digalakkan MgAl_2O_4 -TNR. Sampel mangkin baharu dan yang telah digunakan telah dicirikan oleh pembelauan sinar-X, spektroskopi fotoelektron sinar-X, mikroskopi elektron transmisi resolusi-tinggi, mikroskopi elektron imbasan pancaran medan, Brunauer-Emmett-Teller dengan nitrogen, inframerah transformasi Fourier dan analisis termogravimetri untuk mengkaji tentang penghabluran, keadaan elektronik, permukaan morfologi, struktur liang, keluasan permukaan dan kestabilan. Pada mulanya, analisis termodinamik (TDA) yang sistematik telah dijalankan untuk mengkaji kesan pelbagai parameter proses terhadap komposisi produk keluaran. Keadaan tindak balas keseimbangan yang optimum menurut TDA didapati pada suhu tindak balas 550-750 °C, tekanan 1 atmosfera dan kepekatan fenol 5 wt.%. Ujian aktiviti mangkin bagi Ni/TMP, Ni/TNR dan Ni- Co_3O_4 /TNR telah dilakukan untuk menyiasat peranan Ni dan Co_3O_4 terhadap keberkesanan struktur sokongan TiO_2 yang berbeza terhadap SRP menggunakan reaktor turus tetap tahan karat yang menegak pada 700 °C dan nisbah stim kepada karbon (S/C) adalah 15/1 pada tekanan atmosfera. Selepas pemeriksaan terperinci, mangkin 10%Ni-5% Co_3O_4 /TNR menunjukkan penukaran fenol 92% dan hasil H_2 83.5%. Walaubagaimanapun, penambahan MgAl_2O_4 sebagai sokongan bersama dengan TNR digalakkan oleh Ni/ Co_3O_4 telah didapati sangat berkesan dalam penukaran fenol dengan peningkatan hasil H_2 serta kestabilan yang berpanjangan. Dengan menggunakan mangkin komposit, 96.4% penukaran fenol dengan selektiviti H_2 ~70% dan hasil H_2 88.6% telah dicapai. Parameter yang beroperasi telah disiasat dengan pendekatan statistik menggunakan kaedah tindak balas permukaan (RSM) untuk mendapatkan tindak balas optimum dalam bentuk penukaran fenol dan hasil H_2 . Pengoptimuman SRP oleh RSM mendedahkan bahawa hasil H_2 92.5% dicapai pada keadaan operasi yang optimal pada 781.7 °C, kadar aliran suapan 10.15 ml/jam, kepekatan fenol 7.2 wt.% dan 0.312 g muatan mangkin. Ujian kestabilan menunjukkan aktiviti mangkin komposit berterusan selepas 400 jam. Oleh itu, ini dapat disimpulkan bahawa mangkin MgAl_2O_4 -TNR digalakkan oleh Ni- Co_3O_4 mempunyai potensi yang tinggi untuk kegunaan stim pembentukan semula fenol untuk kaedah pengeluaran hidrogen yang selektif dan mampan.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

A reliable and equitable supply of fuels and chemicals are very important for social and economic development of any society. Currently, the global source of energy generation is mainly dependent on fossil fuels and coal which is 32.9 % and 29.2 %, respectively [1]. Also, utilization of these fossil fuels and hydrocarbons (HCs) causes emission of Greenhouse gases (GHGs) which ultimately effects environment. In addition, with the passage of time these resources will be depleting. In view of the current global stocks versus rate of utilization of oil, coal and gas, these energy sources are anticipated to be drained within next 40, 200 and 70 years, respectively [2].

The current global energy requirement and environmental issues are serious concerns and must be dealt on time; if not, our planet will face an immense energy crises and serious environmental issues. In recent years, a lot of research has been conducted to produce human and environment friendly energy from sustainable and renewable energy resources. The sustainable and renewable energy resources which have been exploited by the researchers for production of renewable energy and renewable fuels are wind, solar thermal, large and small hydro, geothermal and biomass [3].

Recently, hydrogen (H_2) as a sustainable fuel is pursuing much attention to minimize the reliance on fossil fuels because the energy density of H_2 is highest as compared to other fuels and energy sources [4]. Also, H_2 shows zero carbon emission during combustion reaction producing water vapor accompanied by heat in the form of energy [5]. Generally, for large scale H_2 production, nonrenewable sources being used are natural gas (NG), coal and oil. Almost, half of H_2 production is obtained by thermal catalytic reforming and gasification of NG and oils. In addition, heavy naphtha

is the second largest H₂ production sources after coal [6]. A much lower amount which is 4 and 1 % of H₂ is produced from water by electrolysis and biomass, respectively [7]. In short, almost 95% global production of H₂ comes from nonrenewable sources like fossil fuels.

The H₂ generation by sustainable and renewable energy sources like wind energy, biomass, and solar thermal energy are suitable for slowly substituting nonrenewable fossil fuels [8]. Currently, the technologies used in H₂ production are reforming of natural gas (NG) or gasification, electrolysis of water, photo and electro-catalysis of water and photo-fermentation of biomass [9]. Commonly, at industrial scale, H₂ is mainly produced by steam reforming (SR) of HCs, particularly NG as feedstock [10, 11]. On the other hand, SR of HCs is not sustainable because of CO₂ production and nonrenewable nature of fossil fuels feedstock. As compared to conventional production of H₂ by SR of fossil fuels like NG, SR of compounds derived from biomass and bio-oil is close to CO₂ free and so a more reliable and sustainable process. Phenol and phenolic compounds are largely produced from biomass gasification, petrochemical industries, reforming, and waste or in some of the cases as byproduct. Additionally, phenol is the main component of the bio-oil pyrolysis produced by bio-oil refineries. Therefore, phenol could be a suitable feedstock for hydrogen production.

In general, phenolic compounds are produced or separated from renewable/bio-oil sources or from industrial waste contains large amount of water. In pyrolysis of bio oils, approximately 15 to 30 wt. % of water per 30 wt. % phenol is produced [12, 13]. Removal of water from such mixture to get refined phenolic compounds either by physical or chemical means is not an economical approach [14]. Besides, it is difficult to transfer phenolic compounds because they can easily be condensed and can corrode equipment [15]. Similarly, direct transportation of tar having high concentration of phenol causes environmental issues, which is most common in developing countries [16, 17], which ultimately results as a waste of valued organic and renewable fuel resources, in addition of environment pollution.

A lot of exploration has to be done to develop cost effective and environment friendly methods to convert phenols and water mixture into clean fuels and chemicals [18]. There are many techniques for phenol-water conversion like aqueous phase reforming (APR), hydrodeoxygenation (HOX), and steam reforming (SR) [19-21]. The waste heat which is generated during bio-oil gasification, pyrolysis or reforming can be utilized to steam reforming of phenol (SRP). Since, reforming usually require large quantity of water to produce steam, so it is not required to remove water from phenol mixture, hence operation cost and investment is minimized. Purified H₂ rich syngas produced by SRP can be used as renewable fuel or as starting chemical to produce valuable products like methanol [22].

1.2 Steam Reforming of Phenol

Since, reforming usually require large quantity of water to produce steam, so it is not required to remove water from phenol mixture, thus operating cost and investment can be minimized. Purified H₂ rich syngas produced by SRP can be used as renewable fuel or as starting chemical to produce valuable products like methanol [22]. During thermal catalytic SRP, phenol-water mixture reacts to produce high yield of H₂ gas accompanied by other by-products like carbon monoxide (CO), carbon dioxide (CO₂) and water (H₂O). In the SRP, the main reactions are decomposition of phenol-water mixture at high temperature to produce H₂ rich syngas using Equation (1.1). Similarly, water gas shift (WGS) and reverse water gas shift (RWGS) reaction also promoted H₂ production as explained in Equation (1.2) [23, 24]. The overall and complete SRP results in a 14 mole of H₂ per mole of phenol which is maximum theoretical of yield of H₂ as defined in Equation (1.3) [25]



According to Equation (1.3), SRP is favorable at higher steam to phenol (S/P) mole ratios and the reaction equilibrium could be shifted towards right direction resulting in higher phenol conversion, hydrogen yield and product selectivity. However, phenol conversion and hydrogen yield along with other product composition during SRP is not only dependent on reaction temperature. In the case of any homogenous phase reaction system, other reaction conditions such as reactants mole ratios, reactor pressure and inert gas dilution in feed stream are as important as reaction temperature. In order to investigate the effect of the reaction conditions, the thermodynamic analysis is critical to understand further its impact on the product distribution during the reaction [26].

In terms of catalytic performances in SRP, process optimization is important to identify optimum reaction conditions towards achieving the maximum target output and to understand the interaction between input process parameters and output responses such as feed conversion and product yield. To achieve the exact optimum conditions for steam reforming a systematic design of experiments (DOE) has a vital role. Therefore, response surface methodology is mostly used in steam reforming processes for experimental design, optimize and investigate multivariate effect on output product composition in SRP [27].

In catalytic steam reforming of phenol, aluminum oxide (Al_2O_3) is one of the most commonly used support because of its high chemical and mechanical stability, cost-effective and metal dispersion is high because of its high surface area [28]. Furthermore, Ni supported on MgO and Al_2O_3 has showed better performance in terms of conversion of steam reforming of phenol with prevailed H_2 yield [29]. Generally, Ni is commonly used in SR processes because it has low cost relative to other rare earth and noble metals [30]. Noble metals like rhodium (Rh), ruthenium (Ru) and palladium (Pd) can resist carbon formation with increased catalyst stability [31, 32]. However, these metals rare in nature and have high cost which makes them less feasible for commercial use [33]. Although, Ni has a good activity towards C–C bond cleavage, but it has also high rates of methane formation as well as sintering of catalyst along with coke formation [34-36].

In phenol steam reforming, carbon formation can be minimized using bimetallic catalysts like nickel (Ni) and cobalt (Co) on different supports such as, Al_2O_3 , La_2O_3 and ZrO_2 [37]. With addition of Co into Ni containing catalyst, carbon formation and carbon growth can be minimized because Co can break the actual surface on which Ni ensembles, which apparently reduces the particle size of Ni. Moreover, Ni-Co catalyst can enhance stability of catalyst and have better resistance towards oxidation of active metal [23, 38]. Zhao and co-workers [39] reported 68.7 % conversion of ethanol at 350 °C using Ni and Co as catalyst supported on Al_2O_3 for SR of ethanol. It was further stated that higher dispersion of catalyst shows higher stability and lower carbon deposition.

On the other hand, TiO_2 can be a good candidate to use as active metal support because it is high mechanically and chemically stable, economical and large surface area for active metal dispersion, abundantly available in nature and nontoxic [40]. Kho and co-workers [10] used Ni/ TiO_2 for steam reforming of methane and achieved 45 % methane conversion at 500 °C, however, deactivation of catalyst after 54 hour (h) was observed due to carbon deposition. Comparatively, spinel oxides of the type (AB_2O_4) ($\text{A} = \text{Mg, Ca}$) ($\text{B} = \text{Al}$) have been extensively used and proposed as a support in catalytic steam reforming because of their basic nature and resistance to carbon deposition and sintering [41]. Recently, Mizuno and coworkers [42] used MgAl_2O_4 as support along with Ni-Co as catalyst for steam reforming of acetic acid and reported high rate of adsorption and decomposition of species like acetyl and acetate on metal-support interface. Similarly, Katheria and co-workers [43] reported the use of MgAl_2O_4 as a support for Ni catalyst for steam reforming of methane with better resistance towards deactivation of catalysts.

There is no literature on steam reforming of phenol using Ni-Co as a catalyst supported on modified TiO_2 impregnated with MgAl_2O_4 . Besides, TiO_2 has high surface area for active metal dispersion, low-cost and it is abundantly available. MgAl_2O_4 is also highly active in adsorption of reacting species and can give high basicity and thermal stability. Therefore, in this study thermodynamic analysis has been carried out to find optimal range of operating conditions and Ni- Co_3O_4 supported on $\text{TiO}_2/\text{MgAl}_2\text{O}_4$ nanocomposite has been synthesized and tested for SRP to

investigate the combined effect of modified TiO_2 nanorods and MgAl_2O_4 for catalyst stability and selective H_2 production. Finally, the input process parameters were analyzed and optimized for output responses by using response surface methodology approach.

1.3 Problem Statement

Although, H_2 production from steam reforming of phenol (SRP) has great prospects. The main problems in steam reforming of phenol are given as follow:

- (a) Phenol, one of the major aromatic chemical compound and ubiquitous in industrial wastewater effluent from many sectors (i.e. petroleum refineries, synthetic chemical plants, plastics, pulp and paper, textiles, detergent, pesticide and herbicide, and pharmaceutical factories), has become a problematic issue in many developed and developing countries. This is due to its toxicity threats to humans and aquatic life even at low concentration. Steam reforming is one of the effective technology to convert phenol to hydrogen. However, this process requires higher input energy due to endothermic nature of reaction. The stable aromatic cyclic hydrocarbon structure of phenol further requires high temperature for C-C and -C-H bond breakage during steam reforming reaction.
- (b) Due to endothermic nature of reaction, effects of different parameters such as temperature, feed concentration and reactor pressure greatly effects products distribution. Thus, to achieve desired product gas especially H_2 whilst minimizing side reactions is another challenge in this process. Furthermore, during SRP, side reactions decrease thermal efficiency and lower activity (in terms of selectivity and yield of hydrogen). For example, low reaction temperature results in lower H_2 yield and catalyst deactivation due to multiple side reaction and CO production which leads to coke formation on catalyst surface. The extent of all these reactions is normally a function of reaction conditions, i.e. pressure, temperature and feed concentration. However, there is no such information available in literature to select exact parameters values to maximize hydrogen yield with minimum coke formation.

- (c) Steam reforming of phenol is one of the attractive route to convert phenol to hydrogen and other valuable product gas. The advantage of utilizing phenol as feed in SR is that 14 moles of hydrogen can be produced per mole of phenol via complete steam reforming reactions. On the other hand, it also comprises six carbon atoms in one mole of phenol which could lead to catalyst deactivation due to catalyst sintering and coke formation on catalyst surface. Ultimately, it will lead to lower H₂ yield. Therefore, proper selection and design of catalyst system is required to minimize the catalyst deactivation. An effective catalyst design includes the type of active metals which is promoting the reaction and type of support that can provide good surface area as well as minimizing the carbon formation. The most common supports used in SRP reactions are Al₂O₃, MgO and ZrO₂ but they depict catalyst sintering and carbon formation. Among the metals noble and rare earth metals like La, Pt, Rh, Ru and Ce are commonly used to minimize carbon formation and to achieve higher H₂ yield and prolonged catalyst stability. However, utilization of rare and noble metals makes the process uneconomical and commercially unfeasible.

1.4 Research Hypothesis

On the basis of challenges and problems mentioned in above section for phenol steam reforming, proposed hypothesis and solutions are as follow:

- (a) Steam reforming of phenol with excess water content would be effective strategy to recycle waste water for hydrogen production. However, range of different operating parameters can be identified through thermodynamic analysis (TDA). TDA will be useful to identify possible reactions occur in SRP, thus an effective tool to solve and identify the problem related to the feasible range of operating parameters. Also, optimal process conditions for SRP reaction can be obtained by TDA of the operating process parameters on product distribution. Hence, it will be of great interest to apply thermodynamic study in the current system that involves phenol as a feed in steam reforming.

- (b) Catalyst sintering and carbon formation depends on catalyst structure and variation in process parameters and can be reduced by selecting reducible catalyst support. It is hypothesized that TiO_2 as a catalyst support would provide higher metal support interaction to reduce coke formation. This is because TiO_2 has exceptional electronic interfaces between the active metal and support due to its property of being reducible oxide. The efficiency of TiO_2 would be further improved using TiO_2 nanorods (TNR) due to their 1D structure and higher specific surface area. Therefore, using modified-TNR having larger surface area compared to conventional TiO_2 could be efficient to minimize carbon formation and can further improve the activity as catalyst towards SRP due to high dispersion of active metals over 1D structure. The efficiency of TNR would be promising with loading with Ni and Co_3O_4 nanocubes due to their synergistic effects and reducible characteristics.
- (c) The coupling MgAl_2O_4 with TNR as co support would further improve thermal stability, mechanical strength and basicity of catalyst composite. Moreover, the use of Ni- Co_3O_4 as active metals in TNR- MgAl_2O_4 composite would be promising to enhance both yield and selectivity with prolonged stability. The combined effect of TiO_2 NR and MgAl_2O_4 heterojunctions promoted with Ni- Co_3O_4 as bimetallic active catalyst can demonstrate enhanced catalytic activity as compared to individual support. The MgAl_2O_4 can promote water gas shift reaction by inhibit the carbon formation due to its strong basic nature. Therefore, it is imperative to develop a catalyst having high resist to carbon formation, stability and high selectivity towards H_2 .
- (d) The optimization of operating parameters would further be fruitful to maximize H_2 yield and selectivity with improved phenol conversion. This would also be helpful to reduce operating temperature while maximizing catalyst activity and stability.

1.5 Research Objectives

The main goal of this research is to develop a stable and highly active catalyst composite for phenol steam reforming for hydrogen production. The main objectives of this study are:

- (a) To study thermodynamic analysis of SRP for hydrogen production;
- (b) To synthesize and characterize nickel (Ni) and cobalt oxide (Co_3O_4) modified TiO_2 NR and MgAl_2O_4 catalyst for SRP;
- (c) To investigate catalytic activity and stability of $\text{Ni-Co}_3\text{O}_4/\text{TiO}_2\text{-MgAl}_2\text{O}_4$ nanocomposite in SRP for selective H_2 production;
- (d) To optimize operating conditions in SRP using response surface methodology.

1.6 Scope of Study

This research focused on improving catalytic activity and stability of TiO_2 coupled MgAl_2O_4 based nanocomposite and impregnation with nickel and cobalt oxide. The structure of commercially available anatase TiO_2 catalysts was optimized from microparticle to nanorods. The catalytic performance of the best selected catalysts after screening experiments was tested in a fixed bed reactor while varying different parameters. Initially, thermodynamic analysis using Aspen plus simulation software was conducted to set optimum range of operating conditions for SRP process. Finally, response surface methodology was used on optimal catalyst composite to investigate the effect of multiple input process parameters on output response. In this study the overall scope is divided into following four main sections:

- (a) Thermodynamic analysis (TDA) of SRP for hydrogen production was done by using Aspen plus version 8.8 simulation software. Apart from establishing the optimal operating conditions for SRP operation; phenol conversion, hydrogen yield and selectivity for different products was determined.
- (b) The TiO_2 micro-particles (TMP), TiO_2 nanorods (TNR) and MgAl_2O_4 catalyst supports promoted by Nickel (Ni) and Cobalt oxide (Co_3O_4) were synthesized

in this study. The TNR was prepared by single step wet impregnation and hydrothermal method, respectively. The MgAl_2O_4 was prepared by wet chemical co-precipitation method accompanied by hydrothermal method. The catalysts Ni/TMP, Ni/TNR, Ni- Co_3O_4 /TMP, Ni- Co_3O_4 /TNR, and Ni- Co_3O_4 / MgAl_2O_4 /TNR (TMA) were prepared by wetness impregnation. The prepared samples were calcined at different temperatures to activate the catalyst. The prepared samples were characterized by Nitrogen adsorption-desorption (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), H_2 -temperature programmed reduction (H_2 -TPR) and CO_2 -temperature programmed desorption (CO_2 -TPD), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA).

- (c) The catalytic screening was carried out in SRP reaction on homogeneous reaction as well as synthesized catalysts including Ni/TMP, Ni/TNR, Ni- Co_3O_4 /TMP, Ni- Co_3O_4 /TNR, and Ni- Co_3O_4 / MgAl_2O_4 /TNR (TMA), at reaction temperature $700\text{ }^\circ\text{C}$ under atmospheric pressure, where loading of catalyst was kept constant at 0.3 grams, feed flow rate was maintained at 10 ml/h, N_2 flow rate of 20 ml/min, and 5 wt. % phenol was used as feedstock. The product distribution analysis was investigated to obtain the catalytic activity comparison. Consequently, the parametric study in SRP was further studied on selected catalyst based on the high catalytic activity obtained in catalytic screening. The parameters used in this study were temperature (600 - $900\text{ }^\circ\text{C}$), feed flow rate (5-15 ml/h), catalyst loading (0.1-0.3g), and concentration of phenol (5-15 wt. %), while the responses recorded were phenol conversion, hydrogen yield and hydrogen selectivity.
- (d) The optimum conditions of SRP process were evaluated using response surface methodology (RSM) with Statistica software (version 8.0) to design the experiments and to analysis the effect of multivariate input variable on output responses. The independent input variables such as temperature, phenol concentration, feed flow rate and catalyst loading were selected to optimize dependent output responses such as phenol conversion and H_2 yield.

1.7 Significance of Study

This study is important to address the environmental as well as the economic concerns related to the phenol pollutant whereby a sustainable process utilising renewable sources for the production of clean energy carrier of hydrogen is highly desirable. Phenol is widely known as one of the chemically and physically stable aromatic compound, and considered as a harmful pollutant when found in environment. In this study phenol has been successfully converted into the valuable and pollution free source of energy (H_2) by using a commercially viable process of catalytic steam reforming. In this work, hydrogen production from phenol steam reforming process over Ni- Co_3O_4 supported on various support types with different structures and compositions has been thoroughly investigated.

The most significant findings from this research that are highly contributing in the steam reforming of phenol area is the application of TiO_2 as the catalyst support since it has never been reported in SRP process. Besides, different structures of TiO_2 have been explored to find relationship towards the catalytic activity in phenol steam reforming. In addition, the application of dual support combination between TiO_2 and $MgAl_2O_4$ have also been explored other than the metal loading composition of Ni- Co_3O_4 towards the catalytic activity and stability in phenol steam reforming. Up-to-date, the combination of TiO_2 - $MgAl_2O_4$ as catalyst support have never been investigated as well in the steam reforming reactions. Followings are the specific outcomes of this study:

- (a) The thermodynamic analysis of SRP process is helpful to select best process conditions to achieve desired products. Thus, using TDA, number of experiments can be minimized to save energy with minimum waste of catalyst.
- (b) A novel 10%Ni-5% Co_3O_4 /25% $MgAl_2O_4$ - TiO_2 NR nanocatalyst composite was synthesized, characterized and tested under thermodynamically set operating condition, producing exceptional results in terms of phenol conversion, H_2 yield and long run stability. More importantly, a stability of 400 h was achieved without any obvious deactivation and it can be promising catalyst for commercial utilization in steam reforming processes.

- (c) The response surface methodology was helpful to understand the significance and effect of input process variables on phenol conversion and H₂ yield. With RMS, best operating condition with higher H₂ yield with minimum side reactions were obtained. Thus, it is a promising tool to optimize process parameters and can reduce total number of experiments.

1.8 Layout of Thesis

The main aim of this study is to produce hydrogen by catalytic steam reforming of phenol over modified TiO₂-MgAl₂O₄ (TMA) based catalyst in a fixed bed reactor. A detailed investigation and screening of TiO₂ support structure and MgAl₂O₄ loading ratio has been done to reach to the optimal catalyst support. To predict the possible reaction SRP and extend of these reactions, a thorough study on thermodynamic properties has also been conducted. Furthermore, with the help of thermodynamic analysis ideal process conditions have been evaluated for SRP operation. The best screen out and optimal modified TiO₂-MgAl₂O₄ based catalysts were further tested for catalytic activity and stability in terms of phenol conversion, hydrogen yield and selectivity. Moreover, response surface methodology (RSM) was employed to optimize and analysis the effect of multiple input variables on hydrogen yield and phenol conversion. Catalyst preparation, characterization, screening of various catalysts, catalytic activity testing on different operating conditions, thermodynamic analysis and response surface methodology (RSM) are discussed in different chapters. This thesis contains of six chapters.

Research background, problem and research hypothesis, research objectives, scope and significance of this study has been discussed in Chapter 1. A thorough literature review about energy aspects and sources of hydrogen and phenol are discussed in Chapter 2. Furthermore, basic concepts of steam reforming technique and their merits and demerits are also presented. Different types of catalysts used in phenol as well as other oxygenates steam reforming are summarized in tabulated form have been discussed too in literature review. At the last part thermodynamic and process optimization in steam reforming of phenol and other oxygenates has been presented.

Chapter 3 contains research methodology for this study, which includes; details of equipment and materials used, catalyst preparation methods, catalyst characterization techniques, detail and schematic representation of experimental setup, procedure for parametric, thermodynamic and process optimization techniques. All the characterization results of fresh catalyst composites are discussed in Chapter 4. Chapter 5 contains TDA, catalyst screening, parametric experiments on optimal catalysts, post reaction catalyst characterization, process optimization and analysis of variance (ANOVA) by using RSM. At the end, Chapter 6 represents the conclusion of this study and recommendations for future work.

REFERENCES

1. BP, BP Statistical Review of World Energy 2017. 2017: London, UK.
2. Zheng, C.W., Q. Wang, and C.Y. Li, An overview of medium- to long-term predictions of global wave energy resources. *Renewable & Sustainable Energy Reviews*, 2017. 79: 1492-1502.
3. Panwar, N.L., S.C. Kaushik, and S. Kothari, Role of renewable energy sources in environmental protection: A review. *Renewable and Sustainable Energy Reviews*, 2011. 15: 1513-1524.
4. Kapdan, I.K. and F. Kargi, Bio-hydrogen production from waste materials. *Enzyme and Microbial Technology*, 2006. 38: 569-582.
5. Li, J., Z. Zhao, A. Kazakov, and F.L. Dryer, An updated comprehensive kinetic model of hydrogen combustion. *International Journal of Chemical Kinetics*, 2004. 36: 566-575.
6. Venkata Mohan, S., Y. Vijaya Bhaskar, and P.N. Sarma, Biohydrogen production from chemical wastewater treatment in biofilm configured reactor operated in periodic discontinuous batch mode by selectively enriched anaerobic mixed consortia. *Water Research*, 2007. 41: 2652-2664.
7. Das Debabrata and K. Namita, Recent developments in biological hydrogen production processes. *Chemical Industry and Chemical Engineering Quarterly*, 2008. 14: 57.
8. Balat, H. and E. Kırtay, Hydrogen from biomass – Present scenario and future prospects. *International Journal of Hydrogen Energy*, 2010. 35: 7416-7426.
9. Dincer, I. and C. Acar, Review and evaluation of hydrogen production methods for better sustainability. *International Journal of Hydrogen Energy*, 2015. 40: 11094-11111.
10. Kho, E.T., J. Scott, and R. Amal, Ni/TiO₂ for low temperature steam reforming of methane. *Chemical Engineering Science*, 2016. 140: 161-170.
11. Angeli, S.D., L. Turchetti, G. Monteleone, and A.A. Lemonidou, Catalyst development for steam reforming of methane and model biogas at low temperature. *Applied Catalysis B: Environmental*, 2016. 181: 34-46.

12. Zhao, C., J. He, A.A. Lemonidou, X. Li, and J.A. Lercher, Aqueous-phase hydrodeoxygenation of bio-derived phenols to cycloalkanes. *Journal of Catalysis*, 2011. 280: 8-16.
13. Mohan, D., C.U. Pittman, and P.H. Steele, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy & Fuels*, 2006. 20: 848-889.
14. Morf, P., P. Hasler, and T. Nussbaumer, Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. *Fuel*, 2002. 81: 843-853.
15. Constantinou, D.A., M.C. Álvarez-Galván, J.L.G. Fierro, and A.M. Efstathiou, Low-temperature conversion of phenol into CO, CO₂ and H₂ by steam reforming over La-containing supported Rh catalysts. *Applied Catalysis B: Environmental*, 2012. 117: 81-95.
16. Sprynskyy, M., M. Lebedynets, J. Namieśnik, and B. Buszewski, Phenolics occurrence in surface water of the Dniester river basin (West Ukraine): natural background and industrial pollution. *Environmental Geology*, 2007. 53: 67-75.
17. Oostdam, B.L., Tar pollution of beaches in the Indian Ocean, the South China Sea and the South Pacific Ocean. *Marine Pollution Bulletin*, 1984. 15: 267-270.
18. Liu, H., T. Jiang, B. Han, S. Liang, and Y. Zhou, Selective Phenol Hydrogenation to Cyclohexanone Over a Dual Supported Pd–Lewis Acid Catalyst. *Science*, 2009. 326: 1250.
19. Kim, Y.T., J.A. Dumesic, and G.W. Huber, Aqueous-phase hydrodeoxygenation of sorbitol: A comparative study of Pt/Zr phosphate and PtReO_x/C. *Journal of Catalysis*, 2013. 304: 72-85.
20. Trane, R., S. Dahl, M.S. Skjøth-Rasmussen, and A.D. Jensen, Catalytic steam reforming of bio-oil. *International Journal of Hydrogen Energy*, 2012. 37: 6447-6472.
21. Cortright, R.D., R.R. Davda, and J.A. Dumesic, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature*, 2002. 418: 964-967.
22. Rostrup-Nielsen and J. R., New aspects of syngas production and use. *Catalysis Today*, 2000. 63: 159-164.
23. Nabgan, W., T.A.T. Abdullah, R. Mat, B. Nabgan, S. Triwahyono, and A. Ripin, Hydrogen production from catalytic steam reforming of phenol with

- bimetallic nickel-cobalt catalyst on various supports. *Applied Catalysis A-General*, 2016. 527: 161-170.
24. Polychronopoulou, K., A. Bakandritsos, V. Tzitzios, J.L.G. Fierro, and A.M. Efstathiou, Absorption-enhanced reforming of phenol by steam over supported Fe catalysts. *Journal of Catalysis*, 2006. 241: 132-148.
 25. Wang, S.R., Q.J. Cai, F. Zhang, X.B. Li, L. Zhang, and Z.Y. Luo, Hydrogen production via catalytic reforming of the bio-oil model compounds: Acetic acid, phenol and hydroxyacetone. *International Journal of Hydrogen Energy*, 2014. 39: 18675-18687.
 26. Saeed B., K. and M. Tahir, Thermodynamic investigation and experimental analysis on phenol steam reforming towards enhanced H₂ production over structured Ni/ZnTiO₃ nanocatalyst. *Energy Conversion and Management*, 2019. 180: 796-810.
 27. Nabgan, W., T.A.T. Abdullah, R. Mat, B. Nabgan, Y. Gambo, and A. Johari, Evaluation of Reaction Parameters of the Phenol Steam Reforming over Ni/Co on ZrO₂ Using the Full Factorial Experimental Design. *Applied Sciences-Basel*, 2016. 6.
 28. Nabgan, B., Hydrogen production from acetic acid-phenol steam reforming over bimetallic nickel-cobalt supported on lanthanum oxide-gamma aluminum oxide catalyst. 2014, Universiti Teknologi Malaysia, Faculty of Chemical Engineering.
 29. Garbarino, G., E. Finocchio, A. Lagazzo, I. Valsamakis, P. Riani, V.S. Escribano, and G. Busca, Steam reforming of ethanol-phenol mixture on Ni/Al₂O₃: Effect of magnesium and boron on catalytic activity in the presence and absence of sulphur. *Applied Catalysis B: Environmental*, 2014. 147: 813-826.
 30. Tuza, P.V., R.L. Manfro, N.F. Ribeiro, and M.M. Souza, Production of renewable hydrogen by aqueous-phase reforming of glycerol over Ni-Cu catalysts derived from hydrotalcite precursors. *Renewable Energy*, 2013. 50: 408-414.
 31. Izquierdo, U., V. Barrio, K. Bizkarra, A. Gutierrez, J. Arraibi, L. Gartzia, J. Bañuelos, I. Lopez-Arbeloa, and J. Cambra, Ni and Rh Ni catalysts supported on Zeolites L for hydrogen and syngas production by biogas reforming processes. *Chemical Engineering Journal*, 2014. 238: 178-188.

32. Tahir, M., B. Tahir, N.A.S. Amin, and A. Muhammad, Photocatalytic CO₂ methanation over NiO/In₂O₃ promoted TiO₂ nanocatalysts using H₂O and/or H₂ reductants. *Energy Conversion and Management*, 2016. 119: 368-378.
33. Peng, Q.Q., Y.W. Tao, H.J. Ling, Z.Y. Wu, Z.L. Zhu, R.L. Jiang, Y.M. Zhao, Y.L. Wang, C. Ji, X.Z. Liao, A. Vassallo, and J. Huang, Tuning Hydrogen and Carbon Nanotube Production from Phenol Steam Reforming on Ni/Fe-Based Nanocatalysts. *ACS Sustainable Chemistry & Engineering*, 2017. 5: 2098-2108.
34. Zhou, L., L. Li, N. Wei, J. Li, and J.-M. Basset, Effect of NiAl₂O₄ Formation on Ni/Al₂O₃ Stability during Dry Reforming of Methane. *ChemCatChem*, 2015. 7: 2508-2516.
35. Das, S., S. Thakur, A. Bag, M.S. Gupta, P. Mondal, and A. Bordoloi, Support interaction of Ni nanocluster based catalysts applied in CO₂ reforming. *Journal of Catalysis*, 2015. 330: 46-60.
36. Christensen, K.O., D. Chen, R. Lødeng, and A. Holmen, Effect of supports and Ni crystal size on carbon formation and sintering during steam methane reforming. *Applied Catalysis A: General*, 2006. 314: 9-22.
37. Pant, K.K., P. Mohanty, S. Agarwal, and A.K. Dalai, Steam reforming of acetic acid for hydrogen production over bifunctional Ni–Co catalysts. *Catalysis Today*, 2013. 207: 36-43.
38. Djinović, P., I.G. Osojnik Črnivec, B. Erjavec, and A. Pintar, Influence of active metal loading and oxygen mobility on coke-free dry reforming of Ni–Co bimetallic catalysts. *Applied Catalysis B: Environmental*, 2012. 125: 259-270.
39. Zhao, X. and G. Lu, Modulating and controlling active species dispersion over Ni–Co bimetallic catalysts for enhancement of hydrogen production of ethanol steam reforming. *International Journal of Hydrogen Energy*, 2016. 41: 3349-3362.
40. Mulewa, W., M. Tahir, and N.A.S. Amin, MMT-supported Ni/TiO₂ nanocomposite for low temperature ethanol steam reforming toward hydrogen production. *Chemical Engineering Journal*, 2017. 326: 956-969.

41. Sehested, J., J. A.P. Gelten, I. Remediakis, H. Bengaard, and J. K. Nørskov, Sintering of nickel steam-reforming catalysts: Effects of temperature and steam and hydrogen pressures. Vol. 223. 2004. 432-443.
42. Mizuno, S.C.M., A.H. Braga, C.E. Hori, J.B.O. Santos, and J.M.C. Bueno, Steam reforming of acetic acid over MgAl₂O₄-supported Co and Ni catalysts: Effect of the composition of Ni/Co and reactants on reaction pathways. *Catalysis Today*, 2017. 296: 144-153.
43. Katheria, S., A. Gupta, G. Deo, and D. Kunzru, Effect of calcination temperature on stability and activity of Ni/MgAl₂O₄ catalyst for steam reforming of methane at high pressure condition. *International Journal of Hydrogen Energy*, 2016. 41: 14123-14132.
44. Dutta, S., A review on production, storage of hydrogen and its utilization as an energy resource. *Journal of Industrial and Engineering Chemistry*, 2014. 20: 1148-1156.
45. Migliardini, F., O. Veneri, and P. Corbo, Hydrogen and proton exchange membrane fuel cells for clean road transportation. *Journal of Industrial and Engineering Chemistry*, 2011. 17: 633-641.
46. Bocci, E., A. Di Carlo, S.J. McPhail, K. Gallucci, P.U. Foscolo, M. Moneti, M. Villarini, and M. Carlini, Biomass to fuel cells state of the art: A review of the most innovative technology solutions. *International Journal of Hydrogen Energy*, 2014. 39: 21876-21895.
47. Parthasarathy, P. and K.S. Narayanan, Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield – A review. *Renewable Energy*, 2014. 66: 570-579.
48. Hernández, A.N.C., Gas-phase adsorption in dealuminated natural clinoptilolite and liquid-phase adsorption in commercial DAY zeolite and modified ammonium Y zeolite. 2013.
49. Park, L.K.-E., S. Ren, S. Yiacoumi, X.P. Ye, A.P. Borole, and C. Tsouris, Separation of Switchgrass Bio-Oil by Water/Organic Solvent Addition and pH Adjustment. *Energy & Fuels*, 2016. 30: 2164-2173.
50. Tian, M., Lignocellulosic octane boosters. Technische Universiteit Eindhoven, 2016.

51. Artetxe, M., M.A. Nahil, M. Olazar, and P.T. Williams, Steam reforming of phenol as biomass tar model compound over Ni/Al₂O₃ catalyst. *Fuel*, 2016. 184: 629-636.
52. Polychronopoulou, K., C.N. Costa, and A.M. Efstathiou, The steam reforming of phenol reaction over supported-Rh catalysts. *Applied Catalysis A: General*, 2004. 272: 37-52.
53. Polychronopoulou, K., J.L.G. Fierro, and A.M. Efstathiou, The phenol steam reforming reaction over MgO-based supported Rh catalysts. *Journal of Catalysis*, 2004. 228: 417-432.
54. Garbarino, G., C. Wang, I. Valsamakis, S. Chitsazan, P. Riani, E. Finocchio, M. Flytzani-Stephanopoulos, and G. Busca, A study of Ni/Al₂O₃ and Ni-La/Al₂O₃ catalysts for the steam reforming of ethanol and phenol. *Applied Catalysis B: Environmental*, 2015. 174–175: 21-34.
55. Sutton, D., B. Kelleher, and J.R.H. Ross, Review of literature on catalysts for biomass gasification. *Fuel Processing Technology*, 2001. 73: 155-173.
56. Coll, R., J. Salvadó, X. Farriol, and D. Montané, Steam reforming model compounds of biomass gasification tars: conversion at different operating conditions and tendency towards coke formation. *Fuel Processing Technology*, 2001. 74: 19-31.
57. Wang, D., S. Czernik, D. Montané, M. Mann, and E. Chornet, Biomass to Hydrogen via Fast Pyrolysis and Catalytic Steam Reforming of the Pyrolysis Oil or Its Fractions. *Industrial & Engineering Chemistry Research*, 1997. 36: 1507-1518.
58. Fyfe, C.A., M.S. McKinnon, A. Rudin, and W.J. Tchir, Investigation of the mechanism of the thermal decomposition of cured phenolic resins by high-resolution carbon-13 CP/MAS solid-state NMR spectroscopy. *Macromolecules*, 1983. 16: 1216-1219.
59. Li, X.-y., Y.-h. Cui, Y.-j. Feng, Z.-m. Xie, and J.-D. Gu, Reaction pathways and mechanisms of the electrochemical degradation of phenol on different electrodes. *Water Research*, 2005. 39: 1972-1981.
60. Di Michele, A., A. Dell'Angelo, A. Tripodi, E. Bahadori, F. Sánchez, D. Motta, N. Dimitratos, I. Rossetti, and G. Ramis, Steam reforming of ethanol over Ni/MgAl₂O₄ catalysts. *International Journal of Hydrogen Energy*, 2018.

61. Son, I.H., S. Kwon, J.H. Park, and S.J. Lee, High coke-resistance MgAl₂O₄ islands decorated catalyst with minimizing sintering in carbon dioxide reforming of methane. *Nano Energy*, 2016. 19: 58-67.
62. Mei, D., V. Lebarbier Dagle, R. Xing, K.O. Albrecht, and R.A. Dagle, Steam Reforming of Ethylene Glycol over MgAl₂O₄ Supported Rh, Ni, and Co Catalysts. *ACS Catalysis*, 2016. 6: 315-325.
63. Mei, D., V.-A. Glezakou, V. Lebarbier, L. Kovarik, H. Wan, K.O. Albrecht, M. Gerber, R. Rousseau, and R.A. Dagle, Highly active and stable MgAl₂O₄-supported Rh and Ir catalysts for methane steam reforming: A combined experimental and theoretical study. *Journal of Catalysis*, 2014. 316: 11-23.
64. Zarei Senseni, A., M. Rezaei, and F. Meshkani, Glycerol steam reforming over noble metal nanocatalysts. *Chemical Engineering Research and Design*, 2017. 123: 360-366.
65. Lee, J.H., J.Y. Do, N.-K. Park, H.-J. Ryu, M.W. Seo, and M. Kang, Hydrogen production on Pd_{0.01}Zn_{0.29}Mg_{0.7}Al₂O₄ spinel catalyst by low temperature ethanol steam reforming reaction. *Journal of the Energy Institute*, 2018.
66. Charisiou, N.D., G. Siakavelas, K.N. Papageridis, A. Baklavaridis, L. Tzounis, K. Polychronopoulou, and M.A. Goula, Hydrogen production via the glycerol steam reforming reaction over nickel supported on alumina and lanthana-alumina catalysts. *International Journal of Hydrogen Energy*, 2017. 42: 13039-13060.
67. Trane-Restrup, R., S. Dahl, and A.D. Jensen, Steam reforming of ethanol over Ni-based catalysts: Effect of feed composition on catalyst stability. *International Journal of Hydrogen Energy*, 2014. 39: 7735-7746.
68. Trane-Restrup, R., S. Dahl, and A.D. Jensen, Steam reforming of ethanol: Effects of support and additives on Ni-based catalysts. *International Journal of Hydrogen Energy*, 2013. 38: 15105-15118.
69. Trane-Restrup, R. and A.D. Jensen, Steam reforming of cyclic model compounds of bio-oil over Ni-based catalysts: Product distribution and carbon formation. *Applied Catalysis B: Environmental*, 2015. 165: 117-127.
70. Kho, E.T., E. Lovell, R.J. Wong, J. Scott, and R. Amal, Manipulating ceria-titania binary oxide features and their impact as nickel catalyst supports for low temperature steam reforming of methane. *Applied Catalysis A-General*, 2017. 530: 111-124.

71. Rossetti, I., J. Lasso, E. Finocchio, G. Ramis, V. Nichele, M. Signoretto, and A. Di Michele, TiO₂-supported catalysts for the steam reforming of ethanol. *Applied Catalysis A: General*, 2014. 477: 42-53.
72. Zhang, R., C. Huang, L. Zong, K. Lu, X. Wang, and J. Cai, Hydrogen Production from Methanol Steam Reforming over TiO₂ and CeO₂ Pillared Clay Supported Au Catalysts. *Applied Sciences*, 2018. 8.
73. Yang, X., Y. Wang, M. Li, B. Sun, Y. Li, and Y. Wang, Enhanced Hydrogen Production by Steam Reforming of Acetic Acid over a Ni Catalyst Supported on Mesoporous MgO. *Energy & Fuels*, 2016. 30: 2198-2203.
74. Mondal, T., K.K. Pant, and A.K. Dalai, Mechanistic Kinetic Modeling of Oxidative Steam Reforming of Bioethanol for Hydrogen Production over Rh–Ni/CeO₂–ZrO₂ Catalyst. *Industrial & Engineering Chemistry Research*, 2016. 55: 86-98.
75. Nabgan, B., M. Tahir, T.A.T. Abdullah, W. Nabgan, Y. Gambo, R. Mat, and I. Saeh, Ni/Pd-promoted Al₂O₃-La₂O₃ catalyst for hydrogen production from polyethylene terephthalate waste via steam reforming. *International Journal of Hydrogen Energy*, 2017. 42: 10708-10721.
76. Nabgan, B., W. Nabgan, T.A. Tuan Abdullah, M. Tahir, Y. Gambo, M. Ibrahim, and W. Syie Luing, Parametric study on the steam reforming of phenol-PET solution to hydrogen production over Ni promoted on Al₂O₃-La₂O₃ catalyst. *Energy Conversion and Management*, 2017. 142: 127-142.
77. Nabgan, B., T.A.T. Abdullah, M. Tahir, W. Nabgan, Y. Gambo, M. Ibrahim, I. Saeh, and K. Moghadamian, Evaluation of theoretical and experimental mass transfer limitation in steam reforming of phenol-PET waste to hydrogen production over Ni/La-promoted Al₂O₃ catalyst. *Journal of Environmental Chemical Engineering*, 2017. 5: 2752-2760.
78. Matas Güell, B., I.V. Babich, L. Lefferts, and K. Seshan, Steam reforming of phenol over Ni-based catalysts – A comparative study. *Applied Catalysis B: Environmental*, 2011. 106: 280-286.
79. Garbarino, G., A. Lagazzo, P. Riani, and G. Busca, Steam reforming of ethanol–phenol mixture on Ni/Al₂O₃: Effect of Ni loading and sulphur deactivation. *Applied Catalysis B: Environmental*, 2013. 129: 460-472.

80. Shen, C., W. Zhou, H. Yu, and L. Du, Ni nanoparticles supported on carbon as efficient catalysts for steam reforming of toluene (model tar). *Chinese Journal of Chemical Engineering*, 2017.
81. Veiga, S. and J. Bussi, Steam reforming of crude glycerol over nickel supported on activated carbon. *Energy Conversion and Management*, 2017. 141: 79-84.
82. Xing, R., V.L. Dagle, M. Flake, L. Kovarik, K.O. Albrecht, C. Deshmane, and R.A. Dagle, Steam reforming of fast pyrolysis-derived aqueous phase oxygenates over Co, Ni, and Rh metals supported on MgAl₂O₄. *Catalysis Today*, 2016. 269: 166-174.
83. Markevich, M., S. Czernik, E. Chornet, and D. Montané, Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil. *Energy & Fuels*, 1999. 13: 1160-1166.
84. Bartholomew, C.H., Carbon Deposition in Steam Reforming and Methanation. *Catalysis Reviews*, 1982. 24: 67-112.
85. Trimm, D.L., The Formation and Removal of Coke from Nickel Catalyst. *Catalysis Reviews*, 1977. 16: 155-189.
86. Rostrup-Nielsen, J. and D.L. Trimm, Mechanisms of carbon formation on nickel-containing catalysts. *Journal of Catalysis*, 1977. 48: 155-165.
87. Sinfelt, J.H., Specificity in Catalytic Hydrogenolysis by Metals. *Advances in Catalysis*, 1973. Volume 23: 91-119.
88. Lin, J.-H., P. Biswas, V.V. Gulians, and S. Mixture, Hydrogen production by water-gas shift reaction over bimetallic Cu-Ni catalysts supported on La-doped mesoporous ceria. *Applied Catalysis A: General*, 2010. 387: 87-94.
89. Huang, T.-J., T.-C. Yu, and S.-Y. Jhao, Weighting Variation of Water-Gas Shift in Steam Reforming of Methane over Supported Ni and Ni-Cu Catalysts. *Industrial & Engineering Chemistry Research*, 2006. 45: 150-156.
90. Grenoble, D.C., M.M. Estadt, and D.F. Ollis, The chemistry and catalysis of the water gas shift reaction. *Journal of Catalysis*, 1981. 67: 90-102.
91. Mills, G.A. and F.W. Steffgen, Catalytic Methanation. *Catalysis Reviews*, 1974. 8: 159-210.
92. Dobosz, J., M. Małeczka, and M. Zawadzki, Hydrogen generation via ethanol steam reforming over Co/HAp catalysts. *Journal of the Energy Institute*, 2017.

93. Casas-Ledón, Y., L.E. Arteaga-Perez, M.C. Morales-Perez, and L.M. Peralta-Suárez, Thermodynamic analysis of the hydrogen production from ethanol: first and second laws approaches. *ISRN Thermodynamics*, 2012. 2012.
94. Mas, V., R. Kipreos, N. Amadeo, and M. Laborde, Thermodynamic analysis of ethanol/water system with the stoichiometric method. *International Journal of Hydrogen Energy*, 2006. 31: 21-28.
95. Ibrahimoglu, B., T. Nejat Veziroglu, and A. Huseynov, Study of thermodynamic parameters of hydrogen gas by grapho-analytic method. *International Journal of Hydrogen Energy*, 2005. 30: 515-519.
96. Aktas, S., M. Karakaya, and A.K. Avci, Thermodynamic analysis of steam assisted conversions of bio-oil components to synthesis gas. *International Journal of Hydrogen Energy*, 2009. 34: 1752-1759.
97. Xie, H., Q. Yu, K. Wang, X. Shi, and X. Li, Thermodynamic analysis of hydrogen production from model compounds of bio-oil through steam reforming. *Environmental Progress & Sustainable Energy*, 2013. 33: 1008-1016.
98. Montero, C., L. Oar-Arteta, A. Remiro, A. Arandia, J. Bilbao, and A.G. Gayubo, Thermodynamic comparison between bio-oil and ethanol steam reforming. *International Journal of Hydrogen Energy*, 2015. 40: 15963-15971.
99. Constantinou, D.A., J.L.G. Fierro, and A.M. Efstathiou, The phenol steam reforming reaction towards H₂ production on natural calcite. *Applied Catalysis B: Environmental*, 2009. 90: 347-359.
100. Nabgan, W., R. Mat, T.A.T. Abdullah, B. Nabgan, Y. Gambo, and Z.Y. Zakaria, Development of a kinetic model for hydrogen production from phenol over Ni-Co/ZrO₂ catalyst. *Journal of Environmental Chemical Engineering*, 2016. 4: 4444-4452.
101. Myers, R.H. and D.C. Montgomery, *Response surface methodology: process and product optimization using designed experiments*. Vol. 4. 1995: Wiley New York.
102. Gil, M.V., J. Feroso, F. Rubiera, and D. Chen, H₂ production by sorption enhanced steam reforming of biomass-derived bio-oil in a fluidized bed reactor: An assessment of the effect of operation variables using response surface methodology. *Catalysis Today*, 2015. 242: 19-34.

103. Feroso, J., M.V. Gil, B. Arias, M.G. Plaza, C. Pevida, J.J. Pis, and F. Rubiera, Application of response surface methodology to assess the combined effect of operating variables on high-pressure coal gasification for H₂-rich gas production. *International Journal of Hydrogen Energy*, 2010. 35: 1191-1204.
104. Chang, A.C.C., L.S. Chang, C.Y. Tsai, and Y.C. Chan, Steam reforming of gasification-derived tar for syngas production. *International Journal of Hydrogen Energy*, 2014. 39: 19376-19381.
105. Zarei Senseni, A., S.M. Seyed Fattahi, M. Rezaei, and F. Meshkani, A comparative study of experimental investigation and response surface optimization of steam reforming of glycerol over nickel nano-catalysts. *International Journal of Hydrogen Energy*, 2016. 41: 10178-10192.
106. Pan, X., Y. Zhao, S. Liu, C.L. Korzeniewski, S. Wang, and Z. Fan, Comparing Graphene-TiO₂ Nanowire and Graphene-TiO₂ Nanoparticle Composite Photocatalysts. *ACS Applied Materials & Interfaces*, 2012. 4: 3944-3950.
107. Zhang, X., Hydrothermal synthesis and catalytic performance of high-surface-area mesoporous nanocrystallite MgAl₂O₄ as catalyst support. *Materials Chemistry and Physics*, 2009. 116: 415-420.
108. Nguyen, D.B. and W.G. Lee, Analysis of helium addition for enhancement of reactivity between CH₄ and CO₂ in atmospheric pressure plasma. *Journal of Industrial and Engineering Chemistry*, 2015. 32: 187-194.
109. Green, D.W., *Perry's chemical engineers'*. 2008: McGraw Hill.
110. Davidson, S.D., K.A. Spies, D. Mei, L. Kovarik, I. Kutnyakov, X.H.S. Li, V.L. Dagle, K.O. Albrecht, and R.A. Dagle, Steam Reforming of Acetic Acid over Co-Supported Catalysts: Coupling Ketonization for Greater Stability. *ACS Sustainable Chemistry & Engineering*, 2017. 5: 9136-9149.
111. Koskela, P., M. Teirikangas, A. Alastalo, J. Forsman, J. Juuti, U. Tapper, A. Auvinen, H. Seppä, H. Jantunen, and J. Jokiniemi, Synthesis of cobalt nanoparticles to enhance magnetic permeability of metal-polymer composites. *Advanced Powder Technology*, 2011. 22: 649-656.
112. Du, X., Y. Liu, L. Li, W. Chen, and Y. Cui, Synthesis of MgAl₂O₄ spinel nanoparticles via polymer-gel and isolation-medium-assisted calcination. *Journal of Materials Research*, 2014. 29: 2921-2927.

113. Zhang, Y.X., G.H. Li, Y.X. Jin, Y. Zhang, J. Zhang, and L.D. Zhang, Hydrothermal synthesis and photoluminescence of TiO₂ nanowires. *Chemical Physics Letters*, 2002. 365: 300-304.
114. Ekou, T., L. Ekou, A. Vicente, G. Lafaye, S. Pronier, C. Especel, and P. Marécot, Citral hydrogenation over Rh and Pt catalysts supported on TiO₂: Influence of the preparation and activation protocols of the catalysts. *Journal of Molecular Catalysis A: Chemical*, 2011. 337: 82-88.
115. Deshmane, V.G., S.L. Owen, R.Y. Abrokwah, and D. Kuila, Mesoporous nanocrystalline TiO₂ supported metal (Cu, Co, Ni, Pd, Zn, and Sn) catalysts: Effect of metal-support interactions on steam reforming of methanol. *Journal of Molecular Catalysis A: Chemical*, 2015. 408: 202-213.
116. Ferencz, Z., A. Erdőhelyi, K. Baán, A. Oszkó, L. Óvári, Z. Kónya, C. Papp, H.P. Steinrück, and J. Kiss, Effects of Support and Rh Additive on Co-Based Catalysts in the Ethanol Steam Reforming Reaction. *ACS Catalysis*, 2014. 4: 1205-1218.
117. Zheng, Z., C. Sun, R. Dai, S. Wang, X. Wu, X. An, Z. Wu, and X. Xie, Ethanol Steam Reforming on Ni-Based Catalysts: Effect of Cu and Fe Addition on the Catalytic Activity and Resistance to Deactivation. *Energy & Fuels*, 2017. 31: 3091-3100.
118. Shejale, A.D. and G.D. Yadav, Ni–Cu and Ni–Co Supported on La–Mg Based Metal Oxides Prepared by Coprecipitation and Impregnation for Superior Hydrogen Production via Steam Reforming of Glycerol. *Industrial & Engineering Chemistry Research*, 2018. 57: 4785-4797.
119. Nabgan, W., T.A.T. Abdullah, R. Mat, B. Nabgan, A.A. Jalil, L. Firmansyah, and S. Triwahyono, Production of hydrogen via steam reforming of acetic acid over Ni and Co supported on La₂O₃ catalyst. *International Journal of Hydrogen Energy*, 2017. 42: 8975-8985.
120. Molleti, J. and G.D. Yadav, Potassium modified La-Mg mixed oxide as active and selective catalyst for mono-methylation of phenylacetonitrile with dimethyl carbonate. *Molecular Catalysis*, 2017. 438: 66-75.
121. Simanjuntak, F.S.H., V.T. Widayaya, C.S. Kim, B.S. Ahn, Y.J. Kim, and H. Lee, Synthesis of glycerol carbonate from glycerol and dimethyl carbonate using magnesium–lanthanum mixed oxide catalyst. *Chemical Engineering Science*, 2013. 94: 265-270.

122. Gao, N., C. Quan, Z. Ma, and C. Wu, Thermal Characteristics of Biomass Pyrolysis Oil and Potential Hydrogen Production by Catalytic Steam Reforming. *Energy & Fuels*, 2018. 32: 5234-5243.
123. Abou Rached, J., C. El Hayek, E. Dahdah, C. Gennequin, S. Aouad, H.L. Tidahy, J. Estephane, B. Nsouli, A. Aboukaïs, and E. Abi-Aad, Ni based catalysts promoted with cerium used in the steam reforming of toluene for hydrogen production. *International Journal of Hydrogen Energy*, 2017. 42: 12829-12840.
124. Wang, S., F. Zhang, Q. Cai, L. Zhu, and Z. Luo, Steam reforming of acetic acid over coal ash supported Fe and Ni catalysts. *International Journal of Hydrogen Energy*, 2015. 40: 11406-11413.
125. Pu, J., F. Ikegami, K. Nishikado, and E.W. Qian, Effect of ceria addition on Ni Ru/CeO₂ -Al₂ O₃ catalysts in steam reforming of acetic acid. *International Journal of Hydrogen Energy*, 2017. 42: 19733-19743.
126. Ochoa, A., I. Barbarias, M. Artetxe, A.G. Gayubo, M. Olazar, J. Bilbao, and P. Castano, Deactivation dynamics of a Ni supported catalyst during the steam reforming of volatiles from waste polyethylene pyrolysis. *Applied Catalysis B-Environmental*, 2017. 209: 554-565.
127. Meng, J., Z. Zhao, X. Wang, A. Zheng, D. Zhang, Z. Huang, K. Zhao, G. Wei, and H. Li, Comparative study on phenol and naphthalene steam reforming over Ni-Fe alloy catalysts supported on olivine synthesized by different methods. *Energy Conversion and Management*, 2018. 168: 60-73.
128. Karnjanakom, S., G.Q. Guan, B. Asep, X. Du, X.G. Hao, C. Samart, and A. Abudula, Catalytic steam reforming of tar derived from steam gasification of sunflower stalk over ethylene glycol assisting prepared Ni/MCM-41. *Energy Conversion and Management*, 2015. 98: 359-368.
129. Itkulova, S.S., Y.Y. Nurmakanov, S.K. Kussanova, and Y.A. Boleubayev, Production of a hydrogen-enriched syngas by combined CO₂-steam reforming of methane over Co-based catalysts supported on alumina modified with zirconia. *Catalysis Today*, 2018. 299: 272-279.
130. Tao, J., Q. Lu, C.Q. Dong, X.Z. Du, and E. Dahlquist, Effects of electric current upon catalytic steam reforming of biomass gasification tar model compounds to syngas. *Energy Conversion and Management*, 2015. 100: 56-63.

131. Fu, P., W.M. Yi, Z.H. Li, X.Y. Bai, A.D. Zhang, Y.M. Li, and Z. Li, Investigation on hydrogen production by catalytic steam reforming of maize stalk fast pyrolysis bio-oil. *International Journal of Hydrogen Energy*, 2014. 39: 13962-13971.
132. Constantinou, D.A. and A.M. Efstathiou, Low-temperature purification of gas streams from phenol by steam reforming over novel supported-Rh catalysts. *Applied Catalysis B: Environmental*, 2010. 96: 276-289.
133. Polychronopoulou, K., K. Giannakopoulos, and A.M. Efstathiou, Tailoring MgO-based supported Rh catalysts for purification of gas streams from phenol. *Applied Catalysis B: Environmental*, 2012. 111–112: 360-375.
134. Box, G.E., W.G. Hunter, and J.S. Hunter, *Statistics for experimenters*. 1978.
135. Haaland, P.D., *Experimental design in biotechnology*. Vol. 105. 1989: CRC press.