

HYDROGEN PRODUCTION FROM ACETIC ACID-PHENOL STEAM
REFORMING OVER BIMETALLIC NICKEL-COBALT SUPPORTED ON
LANTHANUM OXIDE-GAMMA ALUMINUM OXIDE CATALYST

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To my beloved Prophet *Mohammad SalawatoAllah Aleyh*

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ABSTRACT

Hydrogen has been recognized as a sustainable and renewable energy carrier for the portable application. Acetic acid and phenol are considered as the unwanted product in the bio-oil derived from the pyrolysis of biomass. This study is to propose the catalytic steam reforming of the mixture over bimetallic Nickel-Cobalt (Ni-Co) supported on Lanthanum (III) Oxide (La_2O_3) and gamma-aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$). The scope of works including the catalyst characterization and the catalyst testing in a fixed bed reactor operated at ambient pressure. The catalyst performance tests are carried out in a fixed bed reactor at atmospheric pressure and temperature from 600°C to 800°C to compare the catalyst dilution, feed flow rate in the range of 0.16 to 0.56 mL/min, and the catalyst weight of 0.1 to 0.3 g. The acidity of the prepared catalyst is less than $\gamma\text{-Al}_2\text{O}_3$ but higher than La_2O_3 . The total surface area of the fresh catalyst decreased by exposing in the reaction from 48 to 30 m^2/g . It was found that the maximum feed conversion achieved 99.99% for acetic acid and 95.5% conversion for phenol at 800°C in the effect of temperature by using catalyst dilution of silicone carbide (SiC). Instead, hydrogen yield and mole fraction decreased with the presence of dilution. The highest temperature of 800°C in this study, and the other parameters like 0.2 gram catalyst and 0.36 ml/min flow rate achieved the highest hydrogen gas which was about 98%. It was resulted that the presence of SiC was able to increase the conversion of feed due to extension of residence time but it affected negatively in hydrogen yield. Hydrogen production also increased by increasing of phenol and acetic acid concentration. The catalyst did not show a significant deactivation for the period of study. This catalyst is promising for the real application.

ABSTRAK

Hidrogen telah dikenal pasti sebagai pembawa tenaga mampan dan boleh diperbaharui untuk aplikasi mudah alih. Asid asetik dan fenol dianggap sebagai produk yang tidak diinginkan di dalam bio-minyak yang diperolehi daripada pirolisis biojisim. Kajian ini mencadangkan pembaharuan stim bermangkin campuran terhadap dwi-logam Nikel Cobalt (Ni-Co) yang disokong pada Lantanum (III) Oksida (La_2O_3) dan gamma-aluminium oksida ($\gamma\text{-Al}_2\text{O}_3$). Skop kajian ini merangkumi pencirian pemangkin dan ujian pemangkin di dalam reaktor katil tetap yang beroperasi pada tekanan ambien. Ujian prestasi pemangkin dijalankan di dalam reaktor katil tetap pada tekanan atmosfera dan suhu 600 oC hingga 800 oC untuk membandingkan pencairan pemangkin, kadar aliran suapan antara 0.16 mL/min hingga 0.56 mL/min dan berat pemangkin dari 0.1g hingga 0.3g. Tahap keasidan bagi pemangkin yang disediakan adalah lebih rendah daripada $\gamma\text{-Al}_2\text{O}_3$ tetapi lebih tinggi daripada La_2O_3 . Luas permukaan untuk pemangkin segar berkurangan daripada 48 kepada 30 m²/g kesan penggunaan daripada reaksi. Adalah didapati bahawa penukaran makanann suapan maksimum mencapai 99.99% untuk asid asetik dan 95.5% penukaran untuk fenol pada suhu 800 oC di atas kesan suhu dengan menggunakan pemangkin pencairan. Sebaliknya, pemilihan dan pecahan mol hydrogen berkurang dengan kumunculan pemangkin pencairan. Suhu tertinggi 800 oC dan parameter lain seperti 0.2 gram pemangkin dan 0.36 mL/min kadar aliran menghasilkan gas hidrogen yang tertinggi iaitu sekitar 98% bagi kedua-dua komponen. Adalah ditunjukkan bahawa kehadiran silikon karbida (SiC) mampu meningkatkan asid asetik dan penukaran fenol disebabkan lanjutan masa yang tinggal tetapi ia memberi kesan negatif kepada pemilihan hidrogen. Penyahaktifan pemangkin yang ketara tidak diperhatikan sepanjang masa kajian. Pemangkin tersebut berpotensi untuk penggunaan sebenar.

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LIST OF ABBREVIATIONS

LHSV	Liquid hourly space velocity
S/C	Steam to Carbon ratio
HAc	Acetic acid
FPS	Fuel processing system
ATR	Auto thermal reforming
O ₂ /C	Oxygen to Carbon ratio
HPLC	High performance liquid chromatography
TCD	Thermal conductivity detectors
FID	Flame ionization detectors
RSM	Response Surface Method
SEM	Scanning electron microscopy
TPR	Temperature-programmed reduction
XRD	X-ray diffraction
WGS	Water Gas Shift reaction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Fossil fuels, particularly in the transition area still play a significant role as the world's energy utilization which hints to severe energy tension and ecological problems like contaminant emission and fossil fuel reduction. The exhaustion of the limited fossil fuel as the solicitation of growing energy will get faster. Furthermore, the origination of creating the considerable greenhouse gases (e.g. CO₂ and CH₄), poisonous gases (SO₂, NO_x) and other contaminants are from combustion of fossil fuel, affecting acid rain and universal warming (Mohammed *et al.*, 2011). Hence, employment of an alternative basis for fossil fuel to avoid these threats will be the basic effort in this study.

Necessity for remodeling fossil fuels with alternative energy origins that are safe for the environment, become one of the most significant matters attached with the universal energy requirements. Hydrogen which resulted from fossil fuels containing great potential that used in a tolerable comer energy economy which is a clean energy bearer with excellent thermal quantity. However; by renewable sources like wind, solar and biomass for hydrogen production, it is possible to get a

complete environmental interests of producing energy from hydrogen. For hydrogen generation biomass which plentifully exists can be measured by means of the future resources (Constantinou *et al.*, 2010).

Certain specialists realize a modern hydrogen economics will substitute our present energy markets which will build fundamental energy substructure by substituting today's energy substructures that will be the power of coming world. However, that idea perhaps will not be appreciated up to far in the futurity. Plus, security still a highest importance in all features of hydrogen energy, hydrogen has a brilliant security history and as several other fuels, it is harmless for carrying, storing and consumptions. Security over severe plan and examination of storing and carrying theories, reports by the hydrogen association. Also this association are improving programs and principles for all sorts of hydrogen-related tools (Momirlan and Veziroglu, 2005).

Nowadays hydrogen production is extracted from usual sources namely water, coal gasification, acetic acid, natural gas, ethanol, phenols, butanol, methane, glycerol, naphtha catalytic steam reforming and bio-oil. (Czernik *et al.*, 2002; Hu and Lu, 2010). Steam reforming is the main and easy knowledge for hydrogen generation which is the benefit of this thought; moreover, steam reforming wants lowermost procedure temperature and greater H_2/CO_2 ratio in contrast with dry reforming (DR), partial oxidation (POX) and coal gasification (Fatsikostas *et al.*, 2002; Basagiannis and Verykios, 2006; Constantinou *et al.*, 2010; Bulushev and Ross, 2011).

In this work acetic acid and phenol steam reforming is the offered technique that has selected for hydrogen generation. Phenol is a broadly faced artful contaminant like oil, biocides, painting, coloring factors and medical crafts, which is hard to remove from wastewater. Phenol is one of the greatest challenging tripartition tars molecules affecting erosion in the interior ignition engines,

inflicting meaningfully the waste-water resulting from biomass gasifiers and hence, daunting a costly wastewater action which is recognized as forerunner of naphthalene creation. For reforming of phenols for example usually pure metals are adopted because phenols are more strict to be altered than other components (Shurong Wang, 2014). Phenols are precious chemicals which resulting from biomass pyrolysis oils. They can be applied as mediators in the synthesis of medicines, for the generation of pastes and the synthesis of speciality polymers. This substance from renewable sources, like biomass via fast pyrolysis procedure and more breakdown phenolics in the segment shape, can be manufactured (Žilnik and Jazbinšek, 2012).

Acetic acid is one of the main ingredients in bio-oil up to 32 wt.% since it has been selected as a basis of hydrogen generation and it is one of the greatest delegate elements of the water-solvable section of bio-oil so it is a waste product. With an overall generation (6.94 million tons in 2009), acetic acid is a significant business merchandise chemical. Currently, by applying non-renewable feed, acetic acid is generally formed (65%) over methanol carbonylation. From the pyrolysis oil the separation of acetic acid could rise the financial attraction of the pyrolysis oil worth, because the marketplace fee of acetic acid (0.6 USD/kg, 2009 level) is higher than price estimates for pyrolysis oil (0.18–0.38 USD/kg) considerably (C. B. Rasrendra and Leijenhurst, 2103). Besides, for the reason that one of the main harms as degenerative permanent materials for engine fuel is the acidity of bio-oil so it is not appropriate for engine fuel. Acetic acid in the bio-oil can be detached out and appended amount in others application for dissolving this problem (Takanabe *et al.*, 2004; Weimer, 2004; Medrano *et al.*, 2008).

To raise the reaction rate the Nickel/Cobalt supported on gamma-aluminum oxide and Lanthanum (III) Oxide is applied in the reformer as a catalyst since it has been initiate that Ni and noble based catalysts to hydrogen production were more energetic and elective and offers good hydrogen incomes in acetic acid steam reforming. Likewise, for bio-oil and biomass gasification Ni catalysts which is not

expensive catalyst are promising. To decrease reaction rate and heat production at serious points in the reactors, catalyst dilution has been applied (Hwang and Smith, 2004). Ketonization, water shift reaction, methanation, and thermal analysis reaction are the reactions that might occur through the acetic acid steam reforming which stated in the next chapter of this study (Fatsikostas *et al.*, 2002; Basagiannis and Verykios, 2006; Bulushev and Ross, 2011).

1.2 Problem Statement

Phenol and acid acetic as a source of hydrogen are unwanted products from pyrolysis of biomass for hydrogen production. Acetic acid from bio-oil generation are 30% (Takanabe *et al.*, 2004) and phenol around 38% (Bu *et al.*, 2011) of unwanted component of pyrolysis oil. One of these problems is that during steam reforming process, the high temperature (700 to 1000 °C) needs to use toward high hydrogen production and high acetic acid and phenol conversion. Another problem is the high cost of catalyst due to huge amount usage of catalyst to increase the steam reforming reaction rate. Hence, the selection of low cost catalyst is important for economic process while to ensure the maximum and stability of hydrogen production. Phenol and acetic acid and phenolic compound are not considered as fuel and it is corrosive to the combustion engines. Phenol and other phenolic mixtures which are difficult to tainted by microorganisms and also poisonous to bacterial in the surroundings, were originated high concentration (200-1000 mg/L) in palm oil mill effluent (POME) and issuant from anaerobic action of POME. Additionally, phenolic mixtures have antibacterial and phytotoxic attributes. Another problem is that acetic acid and phenol are soluble in water and separating these component from water is not economical at low concentration thus steam reforming could be the suitable solution for this issue (Matas Güell *et al.*, 2011; Mamimin *et al.*, 2012).

1.3 Objective of This Work

The objectives of the work are:

- i. To characterize the physical and chemical properties of the Ni/Co supported La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$.
- ii. To evaluate the effect of silicone carbide (SiC) as a catalyst dilution on hydrogen production in different temperature.
- iii. To evaluate the effect of catalyst on the acetic acid/phenol steam reforming on various reaction parameters such as temperature, feed flow rate and the acetic acid to phenol ratio.

1.4 Scope of Study

- i. Prepare the 10% (Ni-Co) with supported catalyst (La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$) using an impregnation method.
- ii. Characterize the chemical and physical properties of the catalyst using temperature programmed desorption with NH_3 , temperature programmed reduction-hydrogen (TPR- H_2), and surface area analysis with nitrogen (BET- N_2).
- iii. Employ 0.2 g of silicon carbide (SiC) as a catalyst dilution and mix with 0.2 g of the main catalyst in different temperature beginning from 600 °C to 800 °C and compare the feed conversion and hydrogen production when catalyst dilution was removed.
- iv. Study the effect of reaction temperature on the acetic acid and phenol reforming in the range of 600-800 °C using bimetallic of 5 wt.% cobalt and 5wt.% nickel supported on La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ by using 1 atm of

pressure, 30 mL/min of flow rate of input gas and 800 °C of temperature as the reaction conditions.

1.5 Significant of Research

Nowadays people are seeking for new source of energy instead of fossil fuel because it is very dangerous for the environment and causes global warming. It is also not renewable and will be finish in the early future. Hence hydrogen can be suitable and safe energy carrier. Another importance of the current study is that the phenol and acetic acid are unwanted materials in industry with huge quantity however these components have a high value of hydrogen in their structure. Extra advantage of this work is that there is no research have been done that mix two different component and very few topics had spoken about phenol or acetic acid separately but in contrast this study had mixed this two components. Moreover as stated at the background of the study, steam reforming needs lowest process temperature and greater H_2/CO_2 ratio in contrast with dry reforming (DR), partial oxidation (POX) and coal gasification which can be another significant issue of the current work. Furthermore, catalyst characterization techniques are significant methods in understanding and evaluating the performance of catalyst towards acetic acid and phenol conversion. The study would be qualified to prepare a thought on reducing the catalyst to rise the hydrogen generation besides conversion.

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