CHAPTER I

INTRODUCTION

1.1   Background

Increasing concerns regarding environmental impacts, the soaring price of petroleum products together with the depletion of fossil fuels have prompted considerable research to identify alternative fuel sources. Many possible alternative fuels such as solar, wind, biomass, geothermal, wave, hydrogen cell, gasohol and biodiesel are more attractive. Biodiesel is the one that has been receiving increasing attention due to its less polluting nature and because it is a promising one to be substituted for conventional diesel, which is a fossil fuel leading to a potential exhaustion. Biodiesel fuels have various advantages such as alternative to petroleum-based fuel, renewable fuel, a favorable energy balance, lower harmful emissions and nontoxic fuel that they have drawn much attention recently. Although biodiesel fuels are produced glycerol and other chemicals, glycerol generated is presently applied for example as a ingredient of cosmetics but a further increase in the production of biodiesel on the increase through the building of new bio-refineries worldwide, the crude glycerol by-product becomes a waste problem and pure glycerol is in surplus. [1]
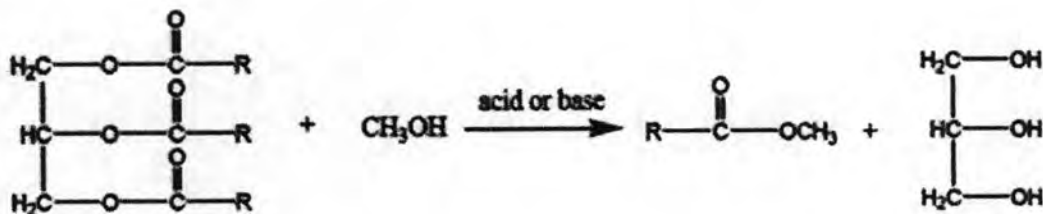
Figure 1.1 Process of biodiesel production [1].

Crude glycerol from the biodiesel process often contains many impurities and is a very poor fuel which is not used in either petrol or diesel engines [2]. It can be purified by distillation to use in both food and pharmaceuticals or can be sent to water

treatment for digestion. However these processes are very expensive and exhibit a low yield [2]. Several alternatives are being explored to utilize crude glycerol and some commercial plants have been established to produce 1,3-propanediol, polyglycerols and polyurethanes from glycerol [3-4]. One mole of glycerol can theoretically produce up to 4 mol of hydrogen gas and in addition, it is possible to get CO as one of the gaseous products due to the high oxygen content. Glycerol as a potential feedstock via pyrolysis, gasification or steam reforming to produce H_2, CO or other fuel gases has received considerable research attention.

1.2 Literature reviews

1.2.1 Glycerol cracking

Chaudhari and Bhakshi attempted to convert glycerol to syngas. They reported that during pyrolysis process, glycerol was converted completely to gas and char at 700°C by steam gasification, 80 wt% of glycerol was converted to gas and produced 92.3 mol% of syn gas with H_2/CO ratio of 2 at 700°C and 10 g/h of steam flow rate. [5]

Stein et al. studied the pyrolysis of glycerol in steam in a laminar flow reactor. The pyrolysis of glycerol without catalyst is a very simple and a cheap method for energy conversion. The initial products of decomposition were CO, acetaldehyde and acrolein and then acetaldehyde and acrolein further decomposed to product primarily CO, CH_4 and H_2. [6]

The thermal decomposition of glycerol in near-critical and supercritical water was also carried out by Buhler et al. in a tubular reactor and a conversion between 0.4% and 31% was observed. They reported the main products of the glycerol degradation including methanol, acetaldehyde, ethanol, CO, CO_2 and H_2. [7]

In 2007, Dalai et al. studied the effects of temperatures in range of 650-800°C, the flow rates of inert gas in the range of 30-70 ml/min and different packing materials (quartz, silicon carbine and sand) in a fixed-bed reactor on the

pyrolysis of glycerol to produce gaseous fuel. The main gas products were CO and H_2 and small amounts of CO_2, CH_4 and C_2H_4. [8]

The use of a catalyst in these pyrolysis processes was much more common than direct thermal cracking. In the literature, Menéndez et al. studied pyrolysis of glycerol over carbonaceous materials to produce synthetic gas. The catalytic effect of two activated carbons was tested and compared with quartz glass chips as packing materials in a fix-bed reactor. The main advantage of using carbonaceous catalyst seems to be its higher selectivity towards hydrogen, resulting in a synthesis gas with a greater H_2/CO ratio. [9]

In the pyrolytic catalytic process, referred to as the Greasoline® process, based on a catalytic conversion reaction over activated carbon, waste fats and oil were internally converted to petrol-quality fuels like propene at temperature of up to 500°C and at ambient pressure. [10]

1.2.2 Glycerol waste cracking

Witchakorn et al. studied the thermal cracking of glycerol to liquid fuels by study in the continuous tubular reactor under the condition of temperature range of 400-600°C feeding rate of a substance starts 1.23-9.45 g/min. At reaction temperature of 500°C, feeding rate of 6.7 g/min gave the highest gasoline fraction of 35.85% whereas kerosene 10.68%, gas oil 29.29% and residue of 24.28% were obtained. [11]

Dupont et al. studied pyrolysis of the crude glycerol from a biodiesel production by thermogravimetry. There were four distinct phases in the pyrolysis process of the crude glycerol. The presence of water and methanol in the crude glycerol and responsible for the first decomposition phase, second phase showed catalyse glycerol decomposition which eventually partically eliminate in two phases upon reaching significantly higher temperature (700 and 970 K). [12]

Hernandez et al. studied heterogeneous cracking reactions of unsaturated acylglyceride model compounds to determine the reaction pathway

towards deoxygenation. Mono-, di-, and triolein were reacted at 400°C over ZSM-5, faujasite, and silica–alumina catalysts. Reactions were carried out using a pulse-type microreactor utilizing online GC analysis. Results indicated the removal of the heteroatom by formation of CO and CO_2. These results reveal the potential of using lipid feedstock for transportation fuels. [13]

1.2.3 Al-SBA-15 catalyst

Stucky *et al.* synthesized well-ordered hexagonal mesoporous silica structure (SBA-15) which was synthesized in acidic media. SBA-15 exhibited pore sized from 50 to 300 angstroms pore volume fractions up to 0.85 and wall thickness of 31 to 64 angstroms. SBA-15 used a variety of poly(alkylene oxide) triblock copolymers and addition of cosolvent organic molecules. [14]

The Al-SBA-15 could be synthesized by incorporating aluminium into SBA-15 *via* direct synthesis and post synthesis. Yue *et al.* studied Al-SBA-15 by direct synthesis and the resulting materials retain the hexagonal order and physical properties of purely siliceous SBA-15. The SBA-15 catalysts exhibited higher catalytic activities in the cumene cracking reaction than Al-MCM-41. [15]

In 2007, Ooi and Bhatia prepared aluminum-containing SBA-15 material using two different methods in order to compare their cracking activity in gasoline production from waste used palm oil. The catalyst prepared *via* direct synthesis possessed disorder pore size distribution whereas the catalyst prepared *via* post-synthesis had narrow pore size distribution. The regenerated Al-SBA-15 prepared *via* post-synthesis gave better activity and yield of gasoline fraction than Al-SBA-15 prepared *via* direct. [16]

1.2.4 Metal supported on SBA-15

A few recent investigations have been published for glycerol conversion over monometallic Ni, Pt, Pd and Ru catalytic systems in many experimental conditions. [17-21]

In accordance with the literature, noble metal catalysts such as Pt and Ru were actived and stable for steam reforming, but they were susceptible to carbon formation. However, the noble metals (Pt, Pd, Ru) cost was the major drawback for their use in industrial applications [22]. For that reason, Ni-based catalysts were generally the most used catalysts for H_2 production by steam reforming of hydrocarbons in industrial-scale. Additionally, more than 130 Pt and Pd bimetallic catalysts were screened for hydrogen production by aqueous-phase reforming (APR) of ethylene glycol solutions using a high-throughput reactor. Promising catalysts were characterized by CO chemisorption and tested further in a fixed bed reactor. Bimetallic PtNi, PtCo, PtFe and PdFe catalysts were significantly more active per gram of catalyst and had higher turnover frequencies for hydrogen production (TOF$_{H2}$) than monometallic Pt and Pd catalysts [23]. Furthermore, The effect of Ni content (1–12 wt%) on the surface and catalytic behavior of bimetallic PtNi catalysts supported on ZSM-5 for reforming of methane with CO_2 was studied. It was shown that addition of a small amount of Pt (0.5%) to Ni catalyst leaded to formation of small nano-sized NiO particles and easy reduction of NiO. It was found that the amount of Ni precursor plays an important role on the surface and catalytic properties of bimetallic catalysts. The improvement of catalytic activity and stability observed for bimetallic catalyst was attributed to an increase of the nickel metallic dispersion caused by an intimate contact between nickel and platinum at Ni-loading of 6 wt% [24].

Blekkan *et al.* prepared and loaded Pt using the deposition-precipitation method (DP) and wet impregnation method on SBA-15. The materials were characterized by N_2 sorption and X-ray diffraction. The N_2 sorption showed that the hydrothermal treatment involved in the DP method has a detrimental effect on the SBA-15 texture so that the final functionalized material contains larger fractions of non-ordered amorphous silica. However, Pt-SBA-15 by DP method exhibited surface area lower than impregnation method. [25]

Kanda *et al.* studied the catalytic activities of various noble metal (Pt, Pd, Rh and Ru) supported on siliceous SBA-15 and Al-containing SBA-15 for hydrodesulfurization (HDS) of thiophene at 350°C. The catalysts were characterized by XRD analysis, N_2 adsorption, 2-propanol dehydration, cumene cracking and FT-

IR. The order of the activities of these catalysts was Pt/SBA-15 > Pd/SBA-15 > Rh/SBA-15 > Ru/SBA-15. [26]

Roberts *et al.* synthesized small Pd nanoparticles by reducing Pd^{2+} ions in a carboxymethlcellulose sodium salt (CMC) or β-D-glucose aqueous solution using sodium borohydride as the reducing agent. The CMC-Pd nanoparticles exhibited farily high catalytic activity for the hydrodechlorination of environmentally deleterious trichloroethene in water. [27]

1.3 Objective

To investigate catalytic performance of Al-SBA-15 and metal supported SBA-15 catalysts in cracking of glycerol and glycerol waste.

1.4 Scopes of work

1. Synthesize SBA-15 under hydrothermal conditions and characterize its physicochemical properties.

2. Synthesize Al-SBA-15 via post synthesis procedure and characterize its physicochemical properties.

3. Prepare metal supported SBA-15 materials by wet impregnation method and characterize theirs physicochemical properties.

4. Study the effects of catalyst type for pure glycerol cracking.

5. Study the effects of reaction temperature, catalyst amount, particle size of metal and position of catalyst for glycerol waste cracking.