CHAPTER I

INTRODUCTION

1.1 Background

The energy consumption is increasing worldwide in recent years. Fossil fuel, one of the major energy resources, is depleting fast, combined with high demand by emerging economies (Figure 1.1). However, these resources produce political and environmental concerns, the crucial source of global warming [1]. In this cause, alternative energy source such as hydrogen, ethanol and biodiesel are being sustained the energy requirement. Biodiesel, an alkyl ester mostly used transesterification process for producing (Figure 1.2), has high potential as liquid transportation fuel because of minimal CO_2 emission when compared to original diesel fuel [2].
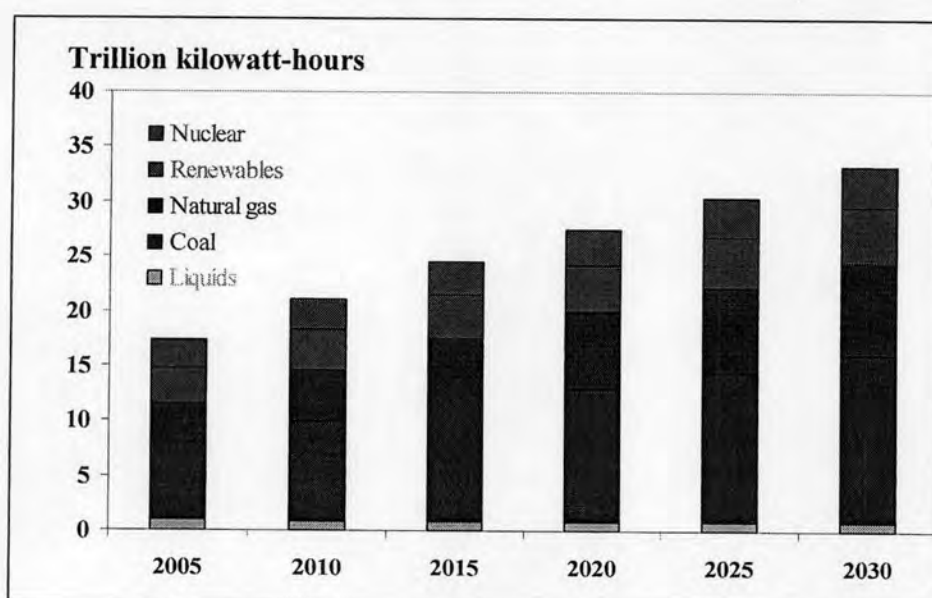

Figure 1.1 World electricity generation by fuel, 2005-2030 [3].

A further increase in the production of biodiesel fuel (Figure 1.3) would raise the problem of efficiently treating waste containing mainly by-product as glycerol. If glycerol contaminated in the alkyl ester-based fuel, it will be separated to another phase which effected to the engine. Moreover, it will be produced high volume of aldehyde [4].
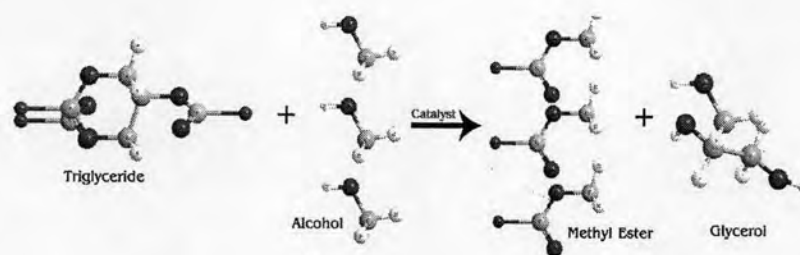
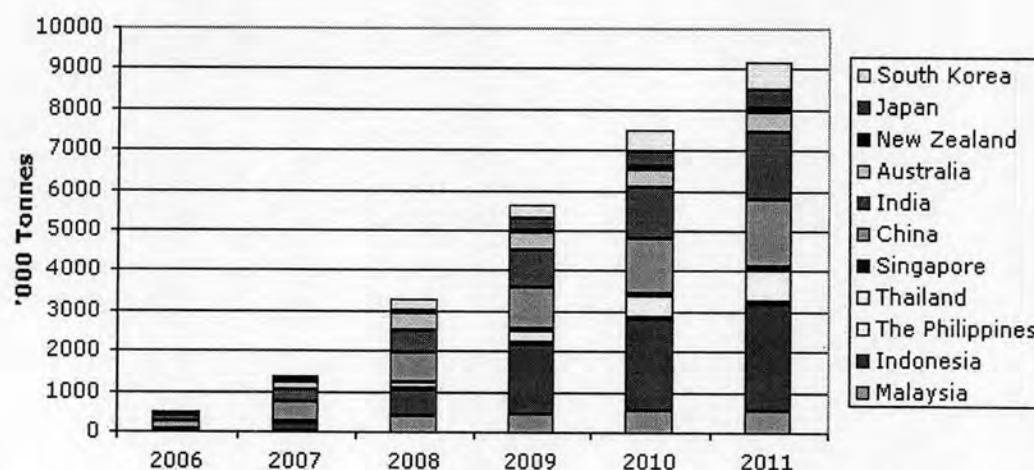**Figure 1.2** Biodiesel production by transesterification process [5].

Figure 1.3 Biodiesel industry: total biodiesel demand (Asia Pacific), 2006-2011 [6].

Crude glycerin or waste from biodiesel production typically contains a mixture of glycerol, methanol, water, inorganic salts, free fatty acids, unreacted mono-, di-, and tri-glyceride, methyl ester, and a variety of other matter organic non-glycerol (MONG) in varying quantities and substantial color (yellow to dark brown) [7-8]. Glycerol purification or separation from biodiesel waste needs an advance technology and high expense for management. In addition, the purified glycerol was circumscribed in cosmetic, pharmaceutics and food industries.

Many researchers tried to utilize glycerol as a potential starting material *via* pyrolysis, gasification or steam reforming to produce synthetic gas (H_2 & CO) or other fuel gas [9-17]. However, there are few papers reported about the management of waste from biodiesel production in catalytic cracking.

1.2 Literature reviews

1.2.1 Glycerol and glycerol waste management

In the past, Antal *et al.* studied the pyrolysis of glycerol in steam using a laminar flow reactor at 650 - 700°C. Gaseous product (carbon monoxide; CO) and liquid products (acetaldehyde and acrolein) were detected in the initial decomposition of glycerol. Liquid products further broke bond to carbon monoxide, ethylene, methane and hydrogen. The overall products of glycerol pyrolysis were carbon monoxide, acetaldehyde, acrolein, hydrogen, ethylene, methane, ethane, carbon dioxide, propylene, and 1,3-butadiene. The initial products were produced from pyrolysis of glycerol *via* bond-cleavage and radical-initiated reactions, whereas the liquid products further decomposed through radical reaction [9].

In 2002, Ederer *et al.* reported ionic reaction and free radical reaction of glycerol in near- and supercritical water. The main products of these reactions are methanol, acetaldehyde, prepionaldehyde, acrolein, allyl alcohol, formaldehyde, carbon monoxide, carbon dioxide and hydrogen. Ionic reaction is preferred at higher pressures and/or higher temperature, whereas the radical reaction is exhibited on lower pressure and/or higher temperature. The reaction model and the kinetic parameter were used to describe the results for glycerol cracking at 450 bar and at the various reaction temperatures from 350°C to 475°C. It was found that the result was consisted both of the ionic and the free radical reactions [10].

Three years later, Nishio et al. studied the production of H_2 and ethanol from glycerol waste after biodiesel manufacturing process using *Enterobacter aerogenes* Hu-101 as culture in packed-bed reactor. The maximum rate of H_2 production from biodiesel waste was 63 mmol/L/h yielding ethanol at 0.85 mol/mol-glycerol [11].

In 2007, Mravec *et al.* studied the effect of catalyst (Amberlyst 15, Amberlyst 35, *p*-toluenesulfonic acid, zeolite H-Y and zeolite H-Beta), solvent (dioxane, dimethyl sulfoxide and sulfolane) and temperature (from 50-90°C) on the etherification of glycerol and ethylene glycol with isobutylene in the liquid phase. The highest conversion of glycerol etherification was performed with *p*-toluenesulfonic acid in sulfolane at 60°C, while the highest conversion of ethylene glycol etherification was exhibited over Amberlyst 35 in dioxane at the same temperature [12].

In the same year, Corma *et al.* reported that catalytic cracking of glycerol and sorbital at 500 - 700°C with six catalysts (a fresh fluid catalytic cracking catalyst; FCC1, an equilibrium fluid catalytic cracking catalyst with metal impurities; ECat, a mesoporous; Al_2O_3, an ultrastable Y zeolite; USY, a ZSM5-based fluid catalytic cracking additive; ZSM5 and an inert silicon carbide; SiC) *via* Diels-Alder and condensation reaction produced olefins, paraffin and coke. It can be concluded that USY and FCC catalysts performed the highest conversion considering gas, coke and aromatic yield. However, ZSM-5 exhibited low coke yield and had the highest yield of olefins and aromatic. In addition, ZSM-5 gave a higher ethylene yield and lower methane yield than the other catalysts [13].

Fernando *et al.* studied hydrogen production of glycerin in steam reforming reaction over nickel-based catalysts with MgO, CeO_2, and TiO_2 supports at 550 - 650°C. This research can be concluded that Ni-based MgO catalyst performed the best catalyst compared to Ni/TiO_2 and Ni/CeO_2 under the temperature of 650°C and H_2 flow rate of 1 mL/min. In addition, at the reaction temperature of 650°C gave higher hydrogen yield than lower reaction temperatures. The highest hydrogen yield, 56.5% was obtained at 650°C with Ni/MgO catalysts [14].

Dalai *et al.* studied the pyrolysed glycerol to producing clean fuel (H_2) or a feedstock of syn gas *via* Fisher-Tropsch synthesis. The various flow rates of N_2 (30 - 70 mL/min), the reaction temperatures (650 - 800°C) and the packing material types (quartz, silicon carbide and sand) and sizes in a tubular reactor at atmospheric pressure were investigated. The mainly products were gas, essentially consisting of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and C_1 - C_2 of hydrocarbon (HC). The maximum yield of gas products (48.6mole% of H_2, 44.9 mole% of CO, 1.0 mole% of CO_2 and the rest of light HC) was carried out at the temperature of 800°C, N_2 flow rate 50mL/min and packing material of quartz particle diameter of 3 - 4 mm [15].

Fernández *et al.* investigated the pyrolysis of glycerol over activated carbon and quartz glass chips as packing materials in fixed-bed reactor for syn-gas production. The major advantage of the previous catalysts was higher selectivity for hydrogen manufacturing. The higher H_2 + CO composition was achieved under microwave heating at 800°C [16].

Ma *et al.* reported that thermodynamic analysis of glycerol dry reforming for hydrogen and synthesis gas production had been performed by the Gibbs free energy minimization method. A function of CO_2 to glycerol ratio, temperature and pressure were investigated parameters. The condition of maximum yield for syn gas production was the temperature of $725^{\circ}C$, CO_2 / glycerol ratio of 1, performing 6.4 mole of syn gas ($H_2 : CO$ =1 : 1) with 33% CO_2 conversion [17].

1.2.2 Characterization of crude glycerol

Yong *et al.* reported that glycerol residue from a palm kernel oil methyl ester plant was characterized with standard testing method. Glycerol residue was achieved after crude glycerol treated with distillation process. The considering parameters were the contents of glycerol, ash, water and matter organic non-glycerol (MONG) including the value of alkalinity. This average composition of glycerol residue was: glycerol 20.2%, ash 64.3%, water 3.0% and MONG 12.4% at pH 12.8 [18].

Ooi *et al.* studied crude glycerin recovery from glycerol residue using standard testing method similar to glycerol residue. It contained 51.4% glycerol, 13.8% ash, 8.9% moisture and 25.9% MONG. These components exhibited higher than glycerol residue because crude glycerin recovery was achieved from glycerol residue treating with chemical or physical management such as acidification with acid, filtration the charred substance, decantation crude fatty acid, neutralization with base solution, etc [19].

Dupont *et al.* investigated thermogravimetric kinetics of crude glycerol. The TG mass loss curves performed four phase in the pyrolysis process consisting of water and some low temperature volatile phase, glycerol phase, degrading impurities phase such as the fatty acid methyl ester, coke and ash at the initial temperature of $50^{\circ}C$, $155^{\circ}C$, $240^{\circ}C$ and $490^{\circ}C$, respectively [20].

1.2.3 Catalytic cracking over Al-SBA-15

From the pervious study, porous material was used in many reactions especially cracking process. Mesoporous hexagonal structure, MCM-41, was successfully synthesize in 1992 [21] because it has pore size between 15 to 100 Å while zeolite has pore size not over 20 Å. Because of this reason, only small molecule can react in zeolite pore, whereas large molecule is able to transfer and react into MCM-41's pore [22].

In 1998, Stucky *et al.* successfully synthesized a mesoporous molecular sieves, SBA-15, using copolymer as template under acidic conditions. SBA-15 has the pore size in the range of 50 to 300 Å, wall thickness about 31 to 64 Å that refers to hydrothermal stability [23]. Many researchers indicated that MCM-41 had lower hydrothermal stability than SBA-15 thus MCM-41 was not suitable for catalytic reaction at high temperature such as cracking. However, the SBA-15 consists of pure silica frameworks which limited to use for acid catalytic application. Generally, incorporation of heteroatom has been implemented in order to create active site and ion-exchange capacity [24].

In 2007, Aguado *et al.* studied the catalytic activity over acid solid catalysts (ZSM-5, zeolite Beta, Al-MCM-41 and Al-SBA-15) relating to its capacity to shift the degradation reaction to the lower temperature. The result showed no effect in the cracking temperature when SiO_2 was used, which confirmed the lack of catalytic activity of non-acid solid catalyst. Although ZSM-5 performed strong acid property, it exhibited a very low catalytic activity on LDPE. The temperature of maximum degradation rate (T_{max}) for LDPE/ZSM-5 was 443°C, only 33°C below the thermal cracking temperature which was attributed to the diffusion impediments that affected the access of bulky molecule of polymer to its internal active sites. T_{max} for LDPE cracking by Al-MCM-41, zeolite Beta, and Al-SBA-15 were remarkably reduced to 407, 417 and 417°C, respectively [25].

Serrano *et al.* reported that the cracking of plastic mixtures, LDPE and ethylene vinyl acetate (EVA) copolymer over nanocrystalline H-ZSM-5, Al-MCM-41 as well as Al-SBA-15. Although nanocrystalline ZSM-5 gave the highest conversion about 80% at 400°C and more than 90% at 420°C, the selectivity to the light oil fraction (C_6-C_{12}) was only about 20%. In contrast, the selectivity to C_6-C_{12} in Al-MCM-41 was 45% and Al-SBA-15 gave the highest selectivity up to 55% of light oil fraction [26].

From these literature reviews, only few researches were studied the management of biodiesel waste by catalytic cracking over mesoporous material in order to increase the value of waste. Thus, this research will be studied on waste from biodiesel production in cracking reaction over SBA-15, Al-SBA-15, catalytic and non-catalytic systems.

1.3 Objective

To study the optimum condition in catalytic cracking of waste from biodiesel production using Al-SBA-15

1.4 Scopes of work

1. Synthesize Al-SBA-15 under hydrothermal conditions with various Si/Al ratios and characterization.

2. Ascertain the composition of waste from biodiesel production as starting material in cracking reaction.

3. Determine the optimum condition for cracking of waste from biodiesel production by studying the effect of Si/Al ratios, temperature and catalyst amounts.