

CHAPTER I

INTRODUCTION

1.1 Background

Majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gases. Diesel fuel is the one fraction from crude oil refinery process containing $C_{14} - C_{25}$ that have an essential function in the industrial economy, transportation and agricultural goods. The diesel fuel demand has been increasing as well as the economic growth. The world diesel consumption is about 100 billion liters per year. Currently, about 2.2 million barrels of diesel fuel is consumed everyday in the U.S. road transportation market. Thailand imports more than 100 million liters of foreign oil each year of which 46% is diesel which is the most consumption. The total world energy consumption and production in 1980-2030 and trend in diesel oil consumption were shown in the Figures 1.1 and 1.2, respectively.

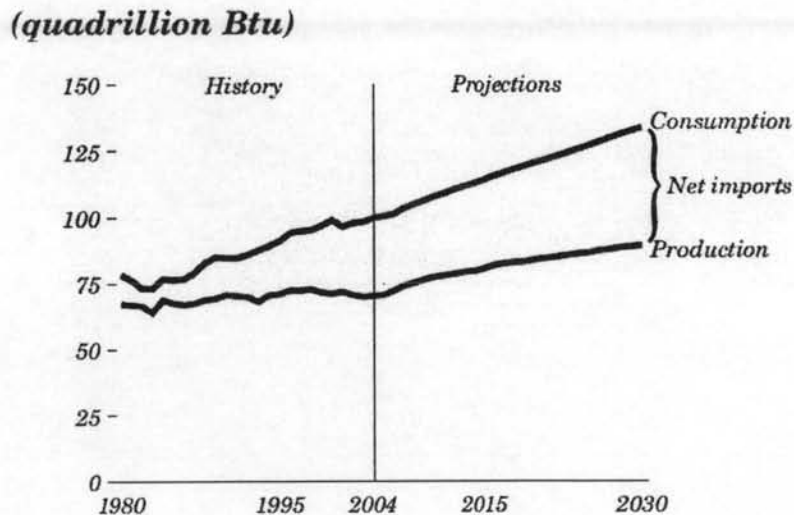


Figure 1.1 The total world energy consumption [1].

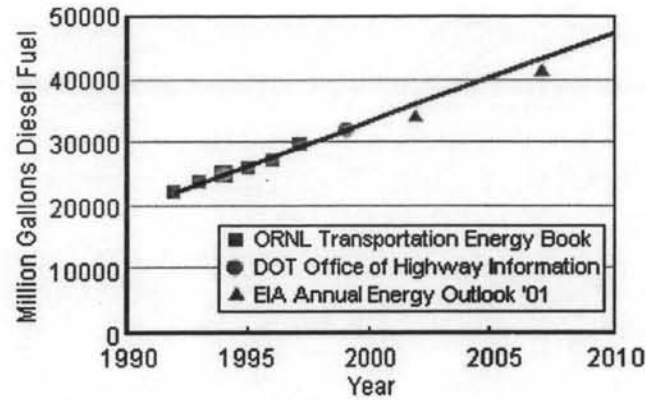


Figure 1.2 Trends in consumption of diesel fuel [2].

At present, the world has been confronted with an energy crisis due to depletion of resources and increased environmental problems. Air pollution is one of the most serious environmental problems all over the world, since NO_x , CO_2 (greenhouse gas) and particulates that are exhausted from diesel engine. This situation has led to search for a clean alternative renewable fuel, which should be not only sustainable but also environment friendly and capable of fulfilling an increasing energy demand. Alternative fuel efforts to improve air quality and increase national energy security through the development of domestic energy sources can be addressed through transportation sector energy consumption. The use of vegetable oils as alternative fuels has been around for 100 years. Vegetable oils occupy a prominent position in the development of alternative fuels although, there have been many problems associated with using it directly in diesel engine (especially in direct injection engine), including;

1. Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices.
2. Carbon deposits.
3. Oil ring sticking.
4. Thickening or gelling of the lubricating oil as a result of contamination by vegetable oil.
5. Lubricating problems.

After that, 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. It is an attractive alternative to petrodiesel fuel due to well-known advantages such as free of sulfur and aromatics, lower dependence on foreign crude oil, biodegradability, low toxicity, and use without engine modifications. Moreover, it reduces the lifecycle of carbon dioxide emissions by almost 70% compared to conventional diesel fuel. The biodiesel market is expected to grow rapidly to meet the new European Directive target of 5.75% volume biofuels in the transport sector

Mostly, biodiesel is prepared from oil feedstocks like soybean oil, rapeseed oil, sunflower oil, palm oil, and animal fat which are comprised of complicate mixtures of triglycerides, TGs (the esters of glycerol with three chains of aliphatic or olefinic FFAs of variable carbons length) and other minor components, such as free fatty acid (FFA), gums, waxes, etc. Biodiesel is usually made through a chemical process called transesterification reaction, whereby triglycerides react with low molecular weight alcohols, typically methanol or ethanol in the presence of catalyst to produce a complex mixture of fatty acid alkyl esters (biodiesel) and glycerol. Catalysts used for the transesterification of triglycerides are classified as homogeneous catalyst, enzyme [3-4] or heterogeneous catalyst, but conventional processing mostly involves an alkali catalyzed process. Because base catalyzed process is less corrosive than the homogeneous acid catalyzed one and proceeds at higher rate. The alkali catalysts including sodium hydroxide, sodium methoxide, potassium hydroxide and potassium methoxide, etc. are effective [5]. However, the alkali catalyst is unsatisfied for low cost high free fatty acid feedstocks due to soap formation. Pretreatment processes using strong acid catalysts have been shown to provide good conversion yields and high quality final products. These techniques have even been extended to allow biodiesel production from feedstocks like soapstock that are often considered to be waste. Even though, homogeneous catalyzed biodiesel production processes are relatively fast and show high conversions with minimal side reactions, they are still not very cost competitive with petrodiesel ones because the catalyst cannot be

recovered and must be neutralized at the end of the reaction. Moreover, the processes are very sensitive to the presence of water and FFAs (Free Fatty Acids).

In the case of enzymatic catalyst, it showed the high selectivity and the enzyme can be immobilized in the support material. However, the enzyme is very expensive and has an unstable activity. The catalyst-free productions were also proposed using supercritical alcohols that require high temperature (475-675 K) [6]. Then biodiesel synthesis using solid catalysts instead of homogeneous liquid catalyst could potentially lead to cheaper production costs because of the reuse of catalyst and substantial reduction of waste and byproduct generation including the opportunity to operate in a continuous process.

ETS-10 is one of heterogeneous basic catalysts which are interesting in transesterification reaction of triglycerides to produce biodiesel because of their structure associated two minus charges per octahedral Ti site, leading to basic catalyst applications and containing suitable pore size (12-membered ring) for starting materials.

1.2 Literature reviews on the ETS-10 catalyst

1.2.1 Synthesis routes of ETS-10 catalyst

Many studies have been carried out to synthesize highly pure ETS-10 materials. In the synthesis routes of ETS-10, many parameters were concerned such as titanium source, fluoride ions, pH of synthesis gel, content of water, Na⁺ and K⁺ ions, SiO₂/TiO₂ molar ratios including synthesis time and temperature on the crystallization of ETS-10. The first report on ETS-10 synthesis was performed by Kuznicki in 1989 [7]. The research presented the synthesis of ETS-10 by using TiCl₃ as the titanium source and presence of ETS-10 seed. The preferred temperature of crystallization was about 100°C to 175°C for a period of time 12 hours to 15 days and the pH of reaction mixture within the range of 9.9 to 10.3.

In 1994, Valtchev and Mintova [8] studied the synthesis of ETS-10 catalyst from titanosilicate gels in the presence of an organic template tetramethylammoniumchloride (TMACl). The aim of the research was to investigate the influence of tetramethylammonium (TMA) on crystallization kinetic of ETS-10. The hydrothermal synthesis was carried out using gels of the following molar

composition 40R: 52Na₂O: 42K₂O: 20TiO₂: 100SiO₂: 7030H₂O where R was TMACl at temperatures of 160, 180, and 200°C. The presence of TMA diminished the nucleation time and accelerated the crystal growth. Moreover, the incorporation of TMA in the channel system of titanium silicate changed the crystal morphology of ETS-10.

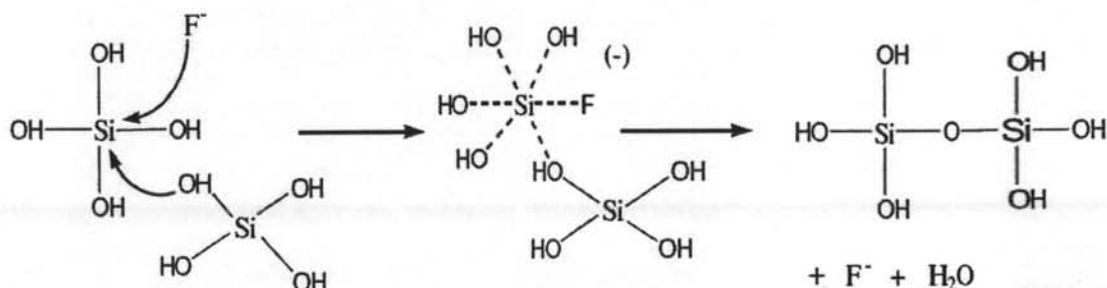
However, the involvement of organic template in catalysts is environmentally undesirable and removal of occluded templates by calcinations may potentially damage the framework of ETS-10. Then in 1996, Sivasanker *et al.* [9] reported the synthesis of ETS-10 over very short reaction time (<16 h) using TiCl₄ as the titanium source in the absence of organic template. The hydrothermal synthesis was carried out with a gel of following molar composition 3.70Na₂O: 0.95K₂O: TiO₂: 5.71SiO₂: 171H₂O and the crystallization were carried out at 473 K with stirrer speed of 300 rpm for 14-16 h. In this synthesis, highly crystalline nearly uniform cuboids of < 1 μm were obtained without any detectable impurity of ETS-4.

In 1998 Anderson *et al.* [10] investigated the hydrothermal synthesis conditions to afford pure and high crystalline ETS-10 from TiCl₃ and TiO₂ (anatase). The influence effect of fluoride ions, temperature, pH of parent gel, sodium and potassium cations, seed and crystallization time have been studied. The optimum temperature and time were 230°C, 15 h (TiCl₃) and 24 h (anatase), respectively. The crystal size of ETS-10 was ranging from 0.5 μm (anatase route) to 25 μm (TiCl₃ route). The first step in TiCl₃ synthesis was the formation of a silica-titania gel which then transforms into ETS-10 and the rate-limiting step of TiO₂ route was the slow dissolution of anatase followed by condensation with silicate species. Seeding with good quality ETS-10 was important when the precursor was TiCl₃, but this was not when anatase was used.

In 2001, Paillaud *et al.* [11] was interested in synthesis of ETS-10 using titanium (IV) fluoride and P25 (a mixture of anatase and rutile) as the titanium source. Pure ETS-10 was obtained with TiF₄ by heating at 200°C for 168 h both with and without organic additive, whereas pure ETS-10 was obtained with P25 at 200°C for 42 h. The influence of fluoride ion, crystallization time, and organic additive were also studied. Small, loosely aggregated ETS-10 crystals up to 1 μm were obtained with

P25. The amorphous TiO_2 contaminate was confirmed by diffuse reflectance UV/VIS. In the presence of organic additive TMACl, the products were large aggregate of 1 μm particle size, whereas 4 μm particle size was obtained in organic free products.

Zhao *et al.* [12] identified the most appropriate conditions in ETS-10 synthesis. To complete the aim, the effect of titanium sources, fluoride ions, pH of synthesis gel, contents of water, $\text{SiO}_2/\text{TiO}_2$ molar ratios, and crystallization temperature and time were examined. It was observed that nano-sized Degussa titanium dioxide (P25) was the best titanium source which promotes highly pure ETS-10 from the synthesis system of $3.4\text{Na}_2\text{O} : 1.5\text{K}_2\text{O} : \text{TiO}_2 : 4.5\text{-}5.5\text{SiO}_2 : 150\text{-}180\text{H}_2\text{O}$ without the presence of organic template. The presence of potassium ions favored the formation of pure ETS-10, due to the structure directing role of potassium ions, but the presence of fluoride ions in synthesis gel resulted in the formation of quartz impurity due to the catalytic role of fluoride ions in polymerization of silicate species.



It was also reported that high quality ETS-10 was able to be obtained in a very narrow pH range (10.4-10.5) and the molar ratio of $\text{SiO}_2/\text{TiO}_2$ must be maintained in a range 4.5-5.5. Otherwise, the crystallization kinetics of ETS-10 can be determined from modified Avrami-Erofeev equation.

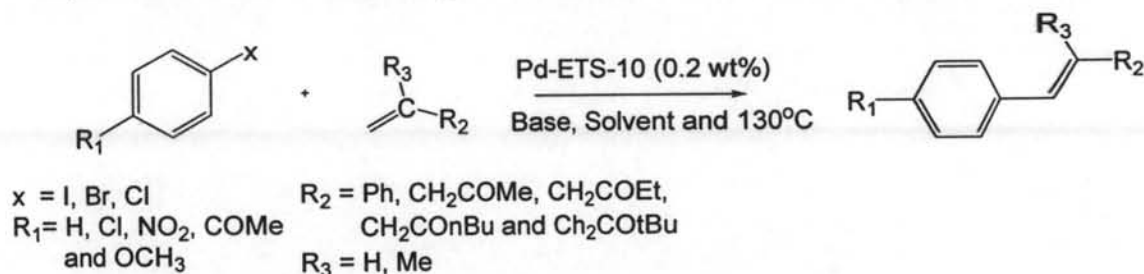
$$\alpha = 1 - \exp[-k(t - t_0)^n]$$

1.2.2 Modification and Application of ETS-10 catalysts

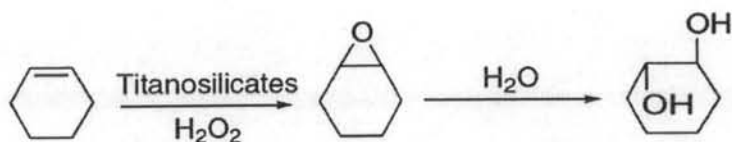
Doskocil *et al.* [14] studied the basic characteristics of various alkali and alkali-earth-exchanged ETS-10 zeolites for the reaction of propylene oxide and carbon dioxide to produce propylene carbonate in the absence of a solvent. The ion-

exchanged ETS-10 catalysts were prepared by using 0.5 M aqueous solution of KOH, CsCl, BaCl₂, MgCl₂ and CaCl₂ at 60°C (30 ml/g) for about 5 h. Adsorption microcalorimetry of adsorbed carbon dioxide was utilized to identify the basic sites of ion-exchanged catalysts. The alkali-exchanged samples were significantly more active than the alkaline earth-exchanged catalysts due to their higher strength CO₂ adsorption sites. Surface basicity associated with the partial charge of the framework oxygen played an important role in the catalyst effectiveness for the reaction. Cs-ETS-10 catalyst exhibited the highest yield for the production of propylene carbonate, presumably due to the higher basicity compared to the other catalysts.

After that, Wagmode *et al.* [15] used palladium-loaded ETS-10 molecular sieve as a catalyst in Heck reaction. The catalyst exhibited high activity and selectivity towards the carbon-carbon coupling of aryl halides with olefins, even at low concentrations of Pd (0.009 to 1.4 mol% with respect to the substrate). In the case of the coupling of ethyl acrylate with iodobenzene, 96% conversion of iodobenzene with greater than 98% selectivity were obtained within 1 h over a 0.2 wt% Pd-loaded catalyst. The reaction was investigated with different alkyl halides, olefins and bases.



In 2004, Tatsumi *et al.* [16] examined the epoxidation ability of ETS-10-derived materials obtained by the post-synthetic treatment with HCl, NH₄Cl and citric acid of various concentrations at room temperature for 4 h at liquid to solid ratio of 100 cm³ to 1 g followed by calcinations. The partially detitanated ETS-10 materials thus prepared proved to be active in the epoxidation of cyclohexene with H₂O₂ as an oxidant due to the formation of tetra coordinated Ti species through the treatment. The highest conversion of cyclohexene and H₂O₂ efficiency was achieved on the catalyst that was treated with 3.7 mol/dm³ NH₄Cl solution followed by the calcination at 723 K.



Anderson *et al.* [17] studied the catalytic performance of microporous titanosilicate ETS-10-type catalysts for the aldol condensation of acetone compared with zeolite X-type materials. The catalysts used were ETS-10, ETAS-10 (substitution with Al), Cs-exchanged ETS-10, Cs₂O-impregnated Cs-ETS-10, Na-X, and ion-exchanged K-X, Cs-X and Cs₂O/Cs-X. The selectivity for final products related to the acid-base character of solid catalyst. The Na-X promoted acid-catalyzed condensation reactions, leading to isobutene as a main product. Conversely, both ETS-10 and chemically treated ETS-10-type materials favored base-catalyzed condensation of acetone, resulting in high selectivity for mesityl oxides as the main product.

1.3 Literature reviews on transesterification reaction of triglycerides

1.3.1 Non-catalytic transesterification reactions

In 1998 Papayannakos *et al.* [18] studied thermal non-catalytic transesterification of soybean oil with methanol. The experiments were carried out at 220 and 235°C at 55 and 62 bar initial pressure with various methanol/oil ratios ranged from 6/1 to 27/1. It was observed that methyl ester content was 85 wt% after 10 h reaction time at 235°C and 67 wt% after 8 h at 220°C. The evolution of the concentration of each component in the ester phase was followed by the kinetic model. A non-catalytic biodiesel production route with supercritical methanol was studied by Ayhan Demirbas [19]. Supercritical methanol has a high potential for both transesterification of triglyceride and methyl esterification of free fatty acids to methyl ester for diesel substitution. In the supercritical method, the yield of conversion increased to 95% in 10 min and the viscosity values of vegetable oil methyl ester were between 3.59 and 4.63 mm²/s. However, the presence of water and free fatty acid affected positively the formation of methyl ester in supercritical method which was opposite to the alkali and acid catalysts.

1.3.2 Transesterification of triglycerides on homogeneous catalysts

Aracil *et al.* [20] compared the homogeneous basic catalysts (sodium hydroxide, potassium hydroxide, sodium methoxide and potassium methoxide) for methanolysis of sunflower oil. All the reactions were carried out at 65°C with a 6:1 molar ratio of methanol to oil and 1 wt% of basic catalyst. The methyl ester concentrations were near 100 wt% over four catalysts. Biodiesel yields after separation and purification steps were higher than 98 wt% for methoxide catalysts, whereas sodium and potassium hydroxide provided 85.9 and 91.67 wt% of biodiesel yield, respectively. The transesterification reaction using NaOH was the fastest, achieving nearly 100 wt% methyl ester concentration at 30 min.

Suarez *et al.* [21] reported the use of $\text{Sn}(3\text{-hydroxy-2methyl-4-pyrone})_2(\text{H}_2\text{O})_2$, $\text{Pb}(3\text{-hydroxy-2methyl-4-pyrone})_2(\text{H}_2\text{O})_2$ and $\text{Zn}(3\text{-hydroxy-2methyl-4-pyrone})_2(\text{H}_2\text{O})_2$ complexes as catalysts in transesterification of alkyl chain triglycerides of various oils from Brazilian's Savannah and Amazonian regions and several alcohols (ethanol, propanol, *iso*-propanol, *n*-butanol, *tert*-butanol and cyclohexanol). All catalytic experiments were carried out using the same molar ratio 400:100:1 for alcohol, vegetable oil and catalyst, respectively at 60°C for 1 h. The Sn and Pb complexes were active for all reactions, independent from the alcohol used. The reaction reactivities decreased with increasing carbonic chain length and when branched alcohols were used, these results strongly suggested that a steric effect controlled the catalytic activity.

Triglyceride contained high free fatty acid (FFA) concentrations was applied as the feedstock in biodiesel production because of the competitive price. Santacesaria *et al.* [22] studied the acetate salts of the following metals: Ca, Ba, Mg, Cd, Mn, Fe, Zn, Co and Ni as catalysts in transesterification of methanol and soybean oil with acidity of 0.2 % w/w. Moreover, the stearates of all above metals were synthesized have also been investigated. The activity of the best catalyst $\text{Pb}(\text{Ac})_2$ was lowered by the water formation during esterification of FFA, it was possible to obtain high fatty acid methyl ester (FAME) yields (96%) and a low final FFA concentration (<1%), in a relatively short reaction time (200 min). The stearates had better

performance than acetates because their higher solubility in the oil phase where the reaction occurs.

1.3.3 Transesterification of triglyceride on heterogeneous catalysts

In 2005, Lee et al. [23] studied the series of MgAl hydrotalcite ($[\text{Mg}_{(1-x)}\text{Al}_x(\text{OH})_2]^{x+}(\text{CO}_3)_{x/n}^{2-}$) materials over the range $x=0.25-0.55$ in biodiesel synthesis. The hydrotalcite structure was shown in Figure 1.3.

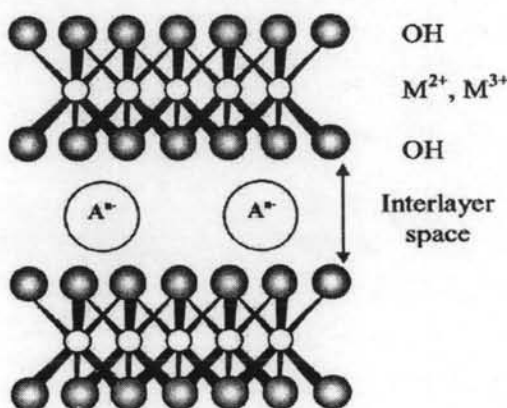
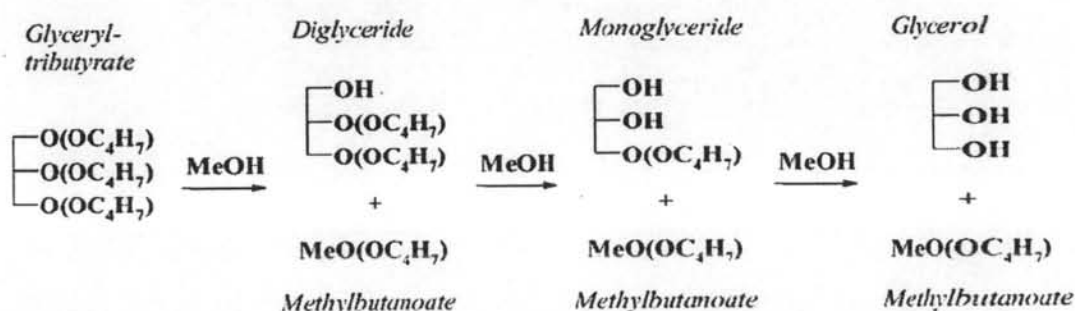


Figure 1.3 Hydrotalcite structure showing the brucite like layers and interlayer anions.

The XRD patterns showed the characteristic of hydrotalcite phase with a steady lattice expansion observed with increasing Mg content. Hydrotalcite catalysts were effective for the liquid phase transesterification reaction of glyceryl tributyrate with methanol. The reactions were performed at 60°C for 3 h. The reaction rate increased steadily with Mg content that also correlates with intralayer electron density which can be associated with increasing basicity.



Lee et al. [24] used the Na/NaOH/ γ -Al₂O₃ heterogeneous base catalyst for the production of biodiesel. The catalyst was prepared by treatment of γ -Al₂O₃ with sodium hydroxide and sodium at 320°C under nitrogen. The formation of the basic sites was studied with XRD, XPS and CO₂-TPD analysis. The transesterification reaction was carried out with the MeOH/oil ratio of 9:1, 60°C under stirring speed 300 rpm for 2 h. A catalyst containing 20 wt% of Na and 20 wt% of NaOH showed the highest activity. A utilization of a co-solvent (*n*-hexane) and oil with a loading amount of 1:5 mol ratio was found to promote the yield in the transesterification of vegetable oils (VO_s) to biodiesel. The Na/NaOH/ γ -Al₂O₃ heterogeneous base catalyst showed almost the same activity under optimized condition compared to the conventional homogeneous NaOH.

Alumina-supported with different potassium compounds were studied as the solid base catalyst in transesterification reaction of soybean oil with methanol. [25] The dependence of the conversion on the reaction variables such as catalyst loading, molar ratio of methanol to oil and reaction time were investigated. The reaction was performed with MeOH/oil ratio of 15:1, catalyst amount of 2 wt%, reaction time 8 h and methanol reflux temperature. The conversion to methyl esters over the catalysts was in the following order: KI/Al₂O₃ > KF/Al₂O₃ > KOH/Al₂O₃ > KNO₃/Al₂O₃ > K₂CO₃/Al₂O₃ > KBr/Al₂O₃. The catalyst with 35 wt% KI loading on Al₂O₃ and calcined at 773 K for 3 h was found to be the optimum catalyst, which gave the highest basicity and the best catalytic activity (87.4% conversion).

Moreover, Zongqiang et al. [26] developed the production of biodiesel from jatropha curcas oil using heterogeneous solid super base catalyst, calcium oxide whose basicity was more than 26.5. The preparation of calcium oxide catalyst was performed by dipping the calcium oxide into ammonium carbonate solution and then calcined at high temperature for 1.5 h. Under the optimum conditions of catalyst calcination temperature of 900°C, reaction temperature of 70°C, reaction time of 2.5 h, catalyst dosage of 1.5% and MeOH/oil molar ratio of 9:1, the oil conversion was 93%.

Anionic ion-exchange resin was conducted as heterogeneous catalyst in transesterification of triolein with ethanol to produce ethyl oleate as a biodiesel. The anion-exchange resins with a lower cross-linking density and a smaller particle size gave a higher reaction rate as well as a high conversion. Before the reaction, the anion-exchange resins were mixed with a 1 M NaOH solution to displace chloride ions with hydroxyl ions. The reactions were performed with mol ratio of triolein to ethanol of 1:10 and the resin weight was in the range of 2.97-37.9 g. Combining the three-step regeneration method, the resin could be repeatedly used without any loss in the catalytic activity [27].

The transesterification of soybean oil with methanol were performed with NaX zeolite, ETS-10 and metal catalysts. The NaX and ETS-10 were exchanged with potassium and cesium whereas NaX also containing occluded sodium oxide and sodium azide. The reactions were carried out at 60°C, 120°C and 150°C for 24 h and mol ratio of oil to alcohol was 1:6. The result showed that the increased conversions were attributed to the higher basicity of ETS-10 zeolites and large pore structures that improved intra-particle diffusion. Conversion to methyl esters in excess of 90% were achieved at temperatures of 150 °C and 120 °C with residence times of 24 h. Pretreating the ETS-10 catalyst at 500 °C for 4 h was instrumental in increasing the activity of the ETS-10 catalyst. Methyl ester yield increased with an increase in temperature and the catalyst was reused without observed loss of activity. Moreover, potassium and cesium exchanged ETS-10 provide lower methyl ester yield than ETS-10 in all temperature [28].

From literatures that were mentioned above, the heterogeneous base catalyst was suitable for transesterification reaction both in catalytic activity and separation process. Thus in this research, the basic heterogeneous catalyst ETS-10 and germanium substituted ETS-10 were chosen as catalyst in transesterification reaction. The reaction was started with palm oil and methanol to produce fatty acid methyl ester (biodiesel). Moreover, Na-loaded ETS-10 was prepared in order to increase the basic strength of catalyst that has the potential to increase the methyl ester yield. The catalytic activities of regenerated and Na-reloaded catalysts were also investigated.

1.4 Objectives

- 1.4.1 To synthesize and characterize ETS-10 catalysts with different silica sources and germanium substituted ETS-10 (ETGeS-10) catalyst.
- 1.4.2 To modify the basic strength of ETS-10 by ion-exchange and impregnation method.
- 1.4.3 To study the catalytic activity of ETS-10, ETGeS-10 and Na-modified ETS-10 in transesterification reaction of palm oil.
- 1.4.4 To investigate the optimum conditions in transesterification reaction.
- 1.4.5 To study the catalytic activity of reused and regenerated catalyst.