

# CHAPTER I

## INTRODUCTION

### 1.1 Background

Nowadays, petrochemical industry is rapidly developed and many countries around the globe are interested in investment of improving the production process. The renewable fuels were interested more and more because of limited supply and environmental contamination of fossil fuels. Biodiesel has become one of the most important alternatives to petroleum-based diesel fuel because of less harmful to environment, non-toxicity and high biodegradability. From U.S. Energy Information Agency numbers showed increasing biodiesel production from January's **Figures 1.1** of 66.3 million gallons to 135.1 million gallons in December 2013. Moreover, world energy consumption is projected to increase by 49 percent per year, from 495 quadrillion Btu in 2007 to 739 quadrillion Btu in 2035, shown in **Figure 1.2**.

U. S. monthly biodiesel production 2011 - 2013

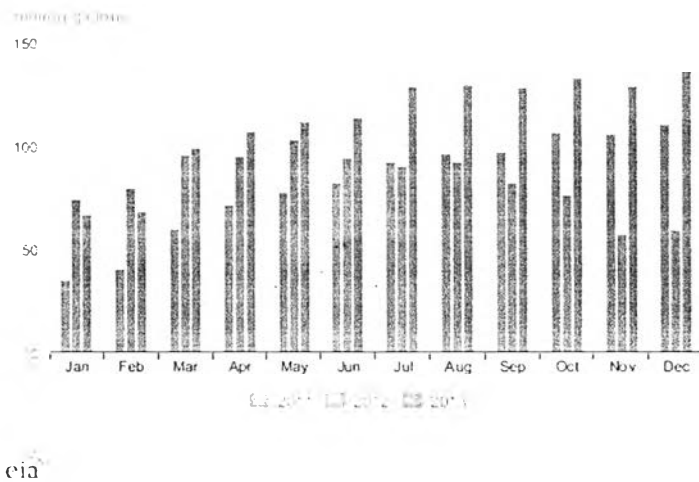


Figure 1.1 The amount of biodiesel production over the past three years [1].

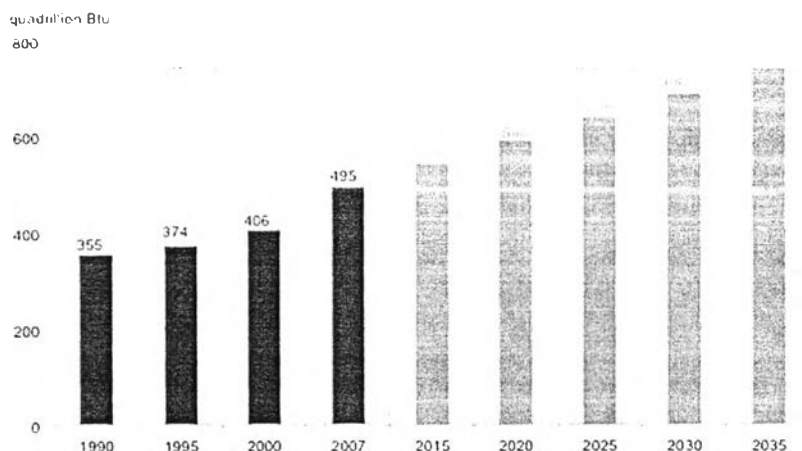


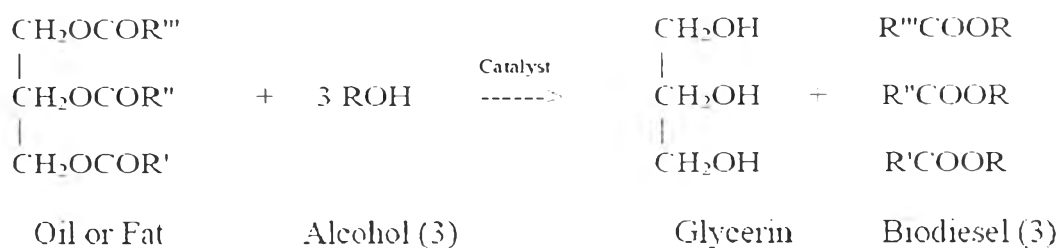
Figure 1.2 World marketed energy consumption, 1990-2035 [2].

The most of the world energy demands are supplied through petrochemical sources. Coal and natural gases, with in exception of hydroelectricity and nuclear energy, of all, these sources are limited and at current usage rates will be consumed shortly. Diesel fuels have an essential function in the industrial economy of a developing country and are used for transport of industrial and agricultural goods, operation of diesel tractor and pump sets in agricultural sector. Economic growth is always accompanied by commensurate increase in the transport. The high-energy demand in the industrialized world as well as in the domestic sector, the increase in diesel prices and environmental concerns causes the widespread use of fossil fuels. It is increasingly necessary to develop the renewable sources of limitless duration and smaller environmental impact than the traditional one.

Thailand has imported crude oil more than 79 percent of all commercial energy. Thailand economy has been influenced when world oil prices increases that mean biodiesel fuel have been campaigned to produce and use for supplant the present diesel. The diesel can be made from raw materials including vegetable oil and used oil from the food industry that have abundantly in many countries. Apart from energy and perspective use of biodiesel, which produced from agricultural products, it can encourage in farmer's occupation as well. Moreover, it also decreases global warming phenomenon and environmental problems.

The main by-product from the industrial biodiesel production, the inter-esterification of oils and fats with methylacetate (Scheme 1.1) [3], is glycerol that is difficult to sell because of market saturation. This situation has inspired a new search

for glycerol uses. The one of different alternative is the use for fuel additives which improves the properties of biodiesel (e.g., diacetin and triacetin, obtained by the esterification of glycerol with acetic acid using acid or base catalyst in Figure 1.3) such as density, kinetic viscosity, cloud point, pour point, cold filter plugging point, dynamic viscosity, cetane number, heating value, distillation curve and flash point [4]. Moreover, the mixture of acylated products has many applications as dyestuffs, as solvents for printing ink, as plasticizers and as softening agents [5].



Scheme 1.1 Reaction of biodiesel production.

Acid or base catalyst is required to increase yield of product by reducing energy of activation (EA) in many reactions. In general, homogeneous catalyst gives a good selectivity or yield and high accessibility but it is hardly separated and recovered from reaction mixture. Thus, heterogeneous catalyst (e.g. exchange resin, zeolite, clay, mesoporous silica) is one of alternative choices to solve this problem. In this research, focus on heterogeneous catalysts cubic *1a-3d* mesoporous silica due to the multi-dimensional channels of large-pore (>5nm), distribution of pore size uniformity, high surface area and high thermal stability. Furthermore, it can be easily separated from product and reusable. Seeing that, these materials have multi-step and long time for preparation. Thus, microwave energy was alternative energy for synthesis of catalyst. Moreover, the synthesized material was increased acidity by sulfonic acid group grafting on the catalyst surface to provide more efficiency.

In this study, the modified household microwave oven was used as an energy source to reduce time for synthesis cubic *1a-3d* mesoporous silica under various synthetic parameters. The synthesized materials from optimal condition was grafting with sulfonic group for using in esterification of glycerol included effect of reaction temperature, mole ratio of glycerol to acetic acid, catalytic amount, reaction time and carbon chain length (caproic acid C<sub>6</sub>, lauric acid C<sub>12</sub> and oleic acid C<sub>18</sub>) on product yield and selectivity.

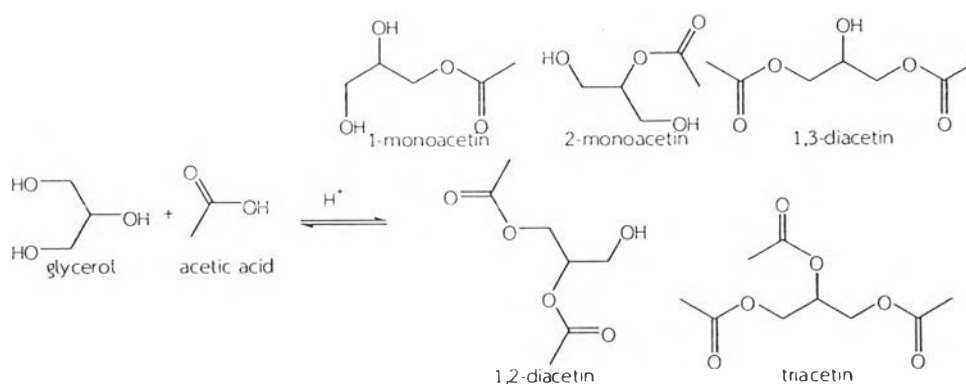


Figure 1.3 Esterification of glycerol with acetic acid.

## 1.2 Literature reviews

This topic was explained into 2 parts, *i.e.* catalytic synthesis and triacetin synthesis in esterification of glycerol.

### 1.2.1 Catalysis synthesis

Landay et al. [6] studied phase transformation of hexagonal mesostructure MCM-41 (*p6mm*) to the cubic (*la-3d*) mesostructure MCM-48 under condition of high pH and aging temperature between 100 and 190°C by using X-ray diffraction (XRD). The cylinder merging, longitudinal linkage of hexagonal pores, and cylinder branching, transvers linkage, are two competing mechanisms proposed for the transformation.

Huang et al. [7] synthesized phenyl-functionalized mesoporous hybrids with *la-3d* structure in acidic condition using co-condensation of tetraethoxysilane (TEOS) and phenyltriethoxysilane (PTES) with Pluronic P123 as structure directing agent. The gel composition mole ratio was 0.017P123 : 0.95TEOS : 0.05PTES : 2.0HCl : 147H<sub>2</sub>O. The range of 3.0 - 8.0% PTES addition to total amount of silicon sources is important role for obtaining cubic structure. Aging temperature between 50-130°C affected to change pore size of cubic *la-3d* mesoporous silica from 4.2 to 8.9 nm. Next two years, they explained that the pre-hydrolysis of PTES prior TEOS adding in the solution is important for the synthesis cubic *la-3d* structure. The catalyst showed higher activity than 2d-hexagonal SBA-15 in the synthesis of flavanone, the product from reaction between phenol and acetone [8].

Xing et al. [9] compared synthesis porous cubic *la-3d* material from carbon and silicon source in micropore range with various aging temperature from 50-130°C. The results showed that increasing aging temperature of synthesis porous cubic *la-3d* silicon affected on elevated pore size from 4.2 nm to 8.9 nm. In contrast, pore size of porous cubic *la-3d* carbon was diminished from 5.0 nm to 3.9 nm when decreasing aging temperature.

Kubota et al. [10] synthesized cubic *la-3d* mesoporous silica from tetraethoxysilane (TEOS) and mercaptopropyltrimethoxysilane (MPTMS) as silicon sources under acidic conditions by using Pluronic P123 as structure directing agent with gel composition mole ratio 1.0 TEOS: 0.089 MPTMS: 0.018 P123: 2.0 HCl: 148 H<sub>2</sub>O. The catalyst was tested to synthesis bisphenol A, reaction of phenol and acetone. From the result, catalyst grafted with mercatopropyl and sulfopropyl group gave the highest % phenol conversion 21.2% with 91.4% selectivity to bisphenol A.

Liu et al.[11] studied the effect of alkyltrimethylammonium bromide with different chain lengths (C<sub>n</sub>H<sub>2n+1</sub>N(CH<sub>3</sub>)<sub>3</sub>Br, *n* = 10, 12, 14 and 16) as template for synthesis silica based mesoporous materials M41S family. It found that, the phase transformation from the hexagonal structure MCM-41 to the cubic structure MCM-48 is depended on increasing of template chain length from C<sub>10</sub> to C<sub>16</sub>.

### 1.2.2 Esterification of glycerol with acetic acid

Troncea et al. 2011 [12] used hydroxylated magnesium fluorides as a catalyst for synthesis triacetin. The activity of catalyst depends on the density of acid site at external surface but the nature of acid site (Lewis and/or Brønsted) influences the selectivity to different acylated products. Using microwave and ultrasound radiation activation methods gave high glycerol conversions (over 90%) and selectivity of included diacetin and triacetin (over 85%).

Gonçalves et al. 2008 [13] described the acetylation of glycerol with acetic acid using different solid acids catalyst such as Amberlyst-15, K-10, Niobic acid, HZSM-5 and HUSY. Amberlyst-15 presented the best performance with the highest conversion (97%) and selectivity to diacetin (54%) and triacetin (13%).

Liao et al. 2009 [14] produced triacetin by two steps, esterification and acetylation using Amberlyst-35 catalyst. The optimum conditions for esterification are temperature 105°C acetic acid to glycerol mole ratio of 9:1 with 0.5 g catalyst. After



4 hr., Adding acetic anhydride to reaction mixture gave 100% triacetin selectivity within 15 min.

Nebel et al. 2008 [15] determined acetylated products by using  $^1\text{H}$  NMR followed by GC investigation. The suitable condition to separate the five acetins as follows:  $125^\circ\text{C}$  for 5 min,  $5^\circ\text{C}/\text{min}$  up to  $200^\circ\text{C}$ , hold 10 min. The order of acetylated products from chromatogram is 1-monoacetin, 2-monoacetin, 1,3-diacetin, 1,2-diacetin and triacetin.

Balaraju et al. 2010 [16] used niobic acid supported tungstophosphoric acid (TPA) catalysts 200 mg in esterification 4 hr.,  $120^\circ\text{C}$  and 1:5 mole ratio of glycerol to acetic acid. The reaction exhibited selectivity of triacetin about 20% with 95% high glycerol conversion.

Khayoon M.S. et al. 2011 [17] used activated carbon treated with sulfonic acid as catalyst in esterification at  $120^\circ\text{C}$ , 3 hr., giving 91% glycerol conversion with a selectivity of 38%, 28% and 34% for mono-, di- and triacetin, respectively.

Rodriguez D. et al. 2012 [18] reported the optimum conditions to synthesize triacetin with various type of ion exchange resin (Amberlyst-15, Amberlyst-36, Dowex 50Wx2, Dowex 50Wx4 and Dowex 50Wx8, with respective crosslinkage equal to 2, 4 and 8%) at  $105^\circ\text{C}$  and 1:8 mol ratio of glycerol to acetic acid. From the result, Amberlyst-36 and Dowex-2 gave high acetic acid conversion with total acetylated products over 80% at briefly reaction time.

### 1.3 Objectives

1.3.1 To synthesize the cubic *la-3d* porous silica heterogeneous catalysts for using in esterification of glycerol with fatty acids

1.3.2 To study the effect of reaction parameters on product yield and product distribution in esterification of glycerol

### 1.4 Scopes of work

1.4.1 Synthesize cubic *la-3d* mesoporous silica via hydrothermal and microwave method

1.4.2 Functionalize cubic *la-3d* mesoporous silica with propyl sulfonic group



1.4.3 Characterize resulting porous materials with XRD, N<sub>2</sub> adsorption-desorption, NH<sub>3</sub>-TPD, SEM and TEM

1.4.4 Determine the reaction parameters of esterification of glycerol affect on yield and selectivity of acetylated products

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|--|--|
| - Type of fatty acid   | acetic acid (C <sub>2</sub> ), caproic acid (C <sub>6</sub> ),<br>lauric acid (C <sub>12</sub> ) and oleic acid (C <sub>18</sub> ) |
| - Type of catalyst   |  |
| Microporous catalyst   | HZSM-5, HMCM-22 and H-Beta   |
| Mesoporous catalyst  | MCA-Pr-SO <sub>3</sub> H, FSM-16-Pr-SO <sub>3</sub> H,<br>SBA-15-Pr-SO <sub>3</sub> H  |
| Commercial catalyst  | Nafion SAC-13, Amberlyst-131 and<br>Amberlyst-15   |
| - Reaction temperature   | 95 - 115°C   |
| - Molar ratio of glycerol to<br>fatty acid                     | 1:3 - 1:15   |
| - Catalytic amount base on total<br>weight of reaction mixture | 0 - 8 wt.%   |
| - Reaction time  | 0.5 - 7 hrs.   |

