

CHAPTER I

INTRODUCTION

The main of energy consumed in the world comes from fossil sources are petroleum, natural gas, and coal. The petroleum sources are very important in the development of industrial growth, transportation, agricultural sector, public utilities, and other basic human needs. At present, the petroleum supplies become crisis as shown in a continuously increasing of oil price. This crisis comes from many reasons for example: high rate of consumption, the fossil sources are limited, manipulate in Middle East, which are the biggest oil producers and complicated techniques in oil and gas drilling, which affect production cost. So finding out an alternative sources is important. Biodiesel is the best available alternative fuel. It is mainly produced from renewable biological sources such as vegetable oil, recycling cooking oil, and animal fats or algae. This fuel is biodegradable, clean energy, low emission, and non-toxic. Moreover, the physical components of biodiesel are similar to regular diesel fuel. These are the reasons why biodiesel plays an important role in alternative energy.

Biodiesel, defined as the mono-alkyl esters of long chain fatty acids. It is obtained by transesterification with a monohydric alcohol known as fatty acid methyl ester (FAME) when use methanol as the alcohol component. Biodiesel is an environmental-friendly product, efficient, clean and can also reduce greenhouse gases, which contribute to global warming. There are many advantages over diesel fuel for example: it is safe, derived from domestic and renewable sources, non-flammable, non-toxic, higher flash point and cetane number, inherent lubricity, lower exhaust emission, low sulfur and aromatic content, and biodegradability. On the other hand, the important disadvantages of biodiesel are lower volumetric energy content, low temperature performance, higher NO_x emission, and lower oxidative stability (Papadopoulos *et al.*, 2010). Chemical structure in FAME molecule that affect properties of biodiesel are chain length, degree of unsaturation, and branching of the chain (Wadumesthrige *et al.*, 2009).

Among the fuel properties of biodiesel, two properties that we concern are oxidative stability and cold flow properties. The oxidative stability depends on the degree of unsaturation of the FAME chain (Wadumesthrige *et al.*, 2009). If raw

material contains higher composition of saturated fatty acid, it performs better oxidative stability. On the other hand, if raw material contains lower composition of saturated fatty acid, the cold flow properties become better. The oxidative stability is the ability to react with oxygen that has an effect on vehicle system by clogging in engine filter or engine pump. And the main problem of cold flow properties happen when oil clotted in the cold weather which impact to the engine.

Therefore, the quality of biodiesel can be improved by partial hydrogenation which is a practical process to upgrade the properties of biodiesel. This process can reduce the content of unsaturated FAME by adding more hydrogen to unsaturated FAME in order to increase the degree of saturation and decrease the amount of double bond. This method can increase the oxidative stability and storage properties; however, it is not influence to cold flow properties (Nikolaou *et al.*, 2009).

Among group VIII metals, palladium (Pd) is the most active and selective metal for the hydrogenation reaction. In 2009, Tamai and coworkers studied the activity of Pd supported on mesoporous activated carbons, they found that Pd particles are mainly supported on mesopores rather than micropores. In 2006, Joongjai and co-worker studied liquid-phase hydrogenation of cyclohexane under mild conditions on Pd/SiO₂ in different organic solvents (benzene, heptanol, and N-Methylpyrrolidone (NMP)) under pressurized carbon dioxide, the result showed that the use of high-pressure CO₂ enhanced the hydrogenation activity of Pd/SiO₂ catalyst. Moreover, type of silica, pore size, and pore structure were found to affect characteristics and catalytic properties of the Pd/SiO₂ catalysts in liquid-phase hydrogenation (Panpranot *et al.*, 2004). From these reasons, palladium supported on silica (Pd/SiO₂) was used as a catalyst because of the high activity and selectivity of Pd metal in hydrogenation reaction. In addition, the macroporosity of SiO₂ support, where Pd can be located inside and big FAME molecule can be easily access.

This present work focus on the partial hydrogenation of polyunsaturated fatty acid methyl esters using Pd supported on silica to upgrade biodiesel properties. The catalysts were prepared by incipient wetness impregnation method. The characteristic of Pd/SiO₂ catalysts with different pore sizes of SiO₂ were characterized by gas chromatograph (GC), X-ray diffraction (XRD), surface area analyzer (SAA). scanning electron microscope with energy dispersive spectrometer

(SEM-EDS), temperature programmed desorption / temperature programmed reduction analyzer (TPD/R/O/-MS), and atomic absorption spectrometer (AAS). The effects of pore size of the silica supports and palladium loading on the partial hydrogenation of polyunsaturated FAMES were studied. Moreover, the effects of temperature and hydrogen partial pressure will be also investigated.