CHAPTER I
INTRODUCTION

1.1 State of Problem

Diesel fuels have an essential function in the industrial economy of the country. They are used in heavy trucks, city transport buses, trains, farm equipment, and etc. Diesel consumption in Thailand is currently at 57.4 million liters/day in March, 2012 (http://www.energy.go.th/?q=node/68). This results in an increase in crude oil and petroleum products imports. Moreover, with the limited petroleum reserves, the fluctuation of crude oil price, and greater environmental concerns from using petroleum-based diesel as a source of energy, from these reasons, it is significant that research and development on the alternative fuel should be carried on in order to replace the petroleum-based diesel. Furthermore, with the reason that Thailand is an agricultural country so the conversion of vegetable oil into biodiesel is one of the promising approaches.

Biodiesel or fatty acid methyl ester (FAME) is usually made from transesterification reaction of triglycerides (the main component in vegetable oil) with methanol. Biodiesel is biodegradable, nontoxic, and essentially free of sulfur and aromatics, with lower emissions of SO_x, CO, un-burnt hydrocarbon and particulate matter as compared to conventional diesel. Moreover, it exhibits a high cetane number, high flash point, and proper viscosity (Meher *et al.*, 2006; Nicoloau *et al.*, 2009). However, some biodiesel properties such as oxidative stability and cold flow properties depend on natural characteristic of starting vegetable oil. Biodiesel produced from vegetable oil that contains more unsaturated fatty acid composition performs worse oxidative stability. In contrast, the higher unsaturated fatty acid composition, the better cold flow property becomes (Sonthisawate *et al.*, 2009). The oxidation of the unsaturated FAMEs produces peroxides, aldehydes, ketones, and acids that change biodiesel properties and affect the combustion process (Nicoloau *et al.*, 2009). Therefore, the saturation of polyunsaturated FAMEs by partial hydrogenation is a promising way to improve its stability and enhance its utilization potential.

Generally, supported noble metal catalysts (Ni, Mo, Pd, Rh, Pt, and etc.) are attractive for liquid phase catalytic hydrogenation, because of many advantages: relatively high activity, mild process conditions, and easy separation (Panpranot *et al.*, 2005). From the works done by many researchers, it was found that palladium (Pd) is the best catalyst for hydrogenation reaction (Rylander, 1970; Jang *et al.*, 2005; Dijkstra, 2006; Beers, 2007; McArdle *et al.*, 2011; Cheng *et al.*, 2012). In addition, having Pd well dispersed is required for a catalyst to have high activity, so Pd is usually prepared on the support to increase its dispersion.

In this study, biodiesel upgrading by the partial hydrogenation of polyunsaturated FAMEs was investigated using supported Pd catalysts. The effect of catalyst preparation, types of reactor and reaction variables, pore size of support, and type of metal were studied. In addition, effect of acidic properties of the support on sulfur tolerance was also investigated. Moreover, the properties of biodiesel product after partial hydrogenation reaction, especially oxidative stability and cold flow properties were also examined.

1.2 Objectives

The main objective of this study was to improve the oxidative stability of biodiesel by partial hydrogenation of polyunsaturated FAMEs and to assess the parameters affecting the performance of the catalyst for partial hydrogenation of polyunsaturated FAMEs. The overall objectives of this work were as follows:

1. To study the effect of catalyst preparation on activity of the catalyst in partial hydrogenation of polyunsaturated FAMEs.

2. To investigate the effect of reactor type and reaction condition on the partial hydrogenation of polyunsaturated FAMEs.

3. To study the effect of pore size of support on the partial hydrogenation of polyunsaturated FAMEs.

4. To elucidate the effect of support acidic properties on sulfur tolerance during the partial hydrogenation of polyunsaturated FAMEs.

5. To study the effect of type of metal on the partial hydrogenation of polyunsaturated FAMEs.

1.3 Scope of Work

In this study, Pd was interested to be used as a catalyst for partial hydrogenation of polyunsaturated FAMEs. In the first part, palm biodiesel fuel (BDF), obtained from Verasuwan Co., Ltd., with small component of polyunsaturated FAMEs was selected as a feed for partial hydrogenation and Pd supported on carbon was interested to be used as a catalyst. The partial hydrogenation was studied in a batch reactor at a fixed reaction conditions. The effects of catalyst preparation including: type of palladium precursor ($PdCl_2$ and $Pd(NO_3)_2.2H_2O$), catalyst calcination condition (calcination atmosphere, calcination temperature, and form of catalyst used), type (activated carbon and carbon aerogel) as well as size of carbon support (≤40 μm, 850 μm, and granule form), were investigated.

After that, the optimum condition for catalyst preparation obtained in the first part was used for preparing the catalysts for further study in the effect of reactor type. In this part, partial hydrogenation of FAMEs in a conventional batch reactor and a continuous flow reactor were compared in term of conversion and *cis-trans* selectivity. The effect of reaction conditions for the operation of continuous flow reactor including: temperature, hydrogen partial pressure, and BDF feed flow rate, was also investigated.

In the third part, the support was change from carbon to silica (SiO_2), which is a mesoporous material in order to compare the effect of support pore size on the accessibility of FAME molecules. The Pd supported on four different pore sizes of SiO_2: 3 nm, 10 nm, 30 nm, and 50 nm, were investigated. Moreover, the source of BDF for partial hydrogenation was change from palm to rapeseed oil, which contains higher composition of polyunsaturated FAMEs, in order to express the clearer partial hydrogenation point of view. Turn over frequency (TOF) and rate constants (k) of each hydrogenation step were investigated to explain pore diffusion of reactant.

Furthermore, the effect of support acidic properties on sulfur tolerance during partial hydrogenation of rapeseed oil derived-FAME was studied. The Pd supported on SiO_2 and acidic supports: SiO_2-Al_2O_3 and Al_2O_3 were investigated. The

TOF and rate constants, k of each hydrogenation step, were considered to explain the activity of each catalyst.

Finally, the effect of metal type: Pd, Pt, and Ni on hydrogenation activity and *cis-trans* selectivity, was studied in the last part. The hydrogenation activity of each catalyst was also studied in terms of TOF.