CHAPTER I

INTRODUCTION

Our civilization has increasingly come to rely on energy especially fossil fuels. Fossil fuel comes from several sources for example, coal, natural gas, and petroleum. Petroleum or oil plays the most important role in developing everything from transportation to commerce and to food supply. In the past few years, however, many researchers found that fossil fuels have finite resources, particularly natural gas and oil, which are not sufficient to sustain the increasing rate of the world's fuel consumption. This problem spreads worldwide and causes crucial results such as continuously increasing of oil prices. Among various ways to solve this problem, alternative energy is a popular option. There are many common types of alternative energy. There are wind energy, solar energy, geothermal energy, hydrogen, biofuel, and bioethanol. For agricultural countries such as Thailand, biodiesel seems appropriate because there are plenty of resources that can be used to produce biodiesel.

Biodiesel or fatty acid methyl ester (FAME) can be manufactured from new and used vegetable oils, animal fats, algae, and recycled restaurant grease with methanol via the transesterification reaction. There are many advantages to using biodiesel. For instance, biodiesel is renewable and biodegradable, ecologically harmless fuel, and nontoxic. Therefore, it is safe to handle, store, and transport. In addition, it has many advantages over petroleum-based diesel, for example, it has lower emissions of greenhouse gases (SO_x and CO), and higher cetane number and flash point. In economic point of view, biodiesel requires easier production process and simple equipment which saves the production costs when compared to petroleum-based diesel production process. Moreover, it is a much better lubricant than petroleum-based diesel and extends engine life.

Although there are a lot of advantages, biodiesel does present some drawbacks. For example, there are very specific problems which raised an attractive issue on enhancing its qualities which are oxidative stability and cold flow properties. These properties strongly depend on the natural characteristics of the starting vegetable oil since different types of vegetable oil give different chemical structures, chain length, branching of the chain, and especially degree of unsaturated compounds. If the vegetable oil contains higher composition of unsaturated fatty acid, the lower oxidative stability is exhibited. On the contrary, if the vegetable oil contains lower composition of unsaturated fatty acid, the lower cold flow properties are performed. The oxidation reaction can affect both physical and chemical properties of biodiesel. It can cause acidity in the fuel and form insoluble gums and sediments that can plug fuel, and degrade engine performance as well. Furthermore, biodiesel which gels in cold weather is an interesting problem related with the cold flow properties because it cannot be used in cold countries and also influences the engine performance.

As of these issues mentioned above, partial hydrogenation of biodiesel is introduced to improve these properties in order to upgrade biodiesel quality. By means of partial hydrogenation reaction, hydrogen atoms take place in the double bond of unsaturated FAME. It helps to saturate the molecule of oil and increases the oxidative stability. In general, noble metals (Ni, Mo, Pd, Pt, Rh, and etc.) are applied in the catalytic partial hydrogenation because of its high activity and selectivity. For industrial scale, nickel (Ni) is mainly used as the metal catalyst because of its lower cost as compared to other metals. For laboratory scale, however, many researchers exhibit that palladium (Pd) catalysts give much more activity than nickel. The platinum (Pt) catalyst, though not as active as the Pd catalysts, produces lower trans fatty acid during hydrogenation (McArdle *et al.*, 2011). In addition, Pd or Pt based-catalysts, due to their high activity, can operate at lower reaction temperatures than Ni (M *et al.*, 2011). For solid support, mesoporous silica (SiO_2) is utilized because it has an adequate degree of porosity for transferring the bulky triglyceride molecules and hydrogen to active sites on the catalysts. This may lead to an increase in the activity of the catalysts. Also, silica is inexpensive and reusable. It is highly robust and has higher long term stability compared with the zeolitic materials. Therefore, mesoporous silica is the proper solid support for partial hydrogenation of polyunsaturated FAMEs. Moreover, it is well known that sulfur compound presents in feedstock of biodiesel influent to catalyst especially Pt group (Pd and Pt). From this point, the effect of sulfur compound is also concerned.

One of the goals of this work is to upgrade biodiesel properties by partial hydrogenation of polyunsaturated FAMEs using different metals; Ni, Pd, and Pt, on mesoporous SiO_2 support. According to the compositions of soybean oil, it is selected as feedstock for biodiesel production. Soybean oil has by iodine values of 121–143 g I_2/100 g, which is relatively high as compared to the other oils such as palm and rapeseed oil (Janssen and Rutz, 2008). From this point, it would make the study of partial hydrogenation reaction to be clearer. This work is focus on the effect of various metals on the performance of catalysts which are activity and selectivity to cis-trans. The dispersion of metals on support, size of catalysts, and surface area of catalysts will be studied as well. Additionally, the sulfur tolerance is examined in order to compare the activity of catalysts between the regular biodiesel and sulfur content in biodiesel. Moreover, the important properties of partial hydrogenated biodiesel, particularly oxidative stability and cold flow properties will be investigated.