CHAPTER I

INTRODUCTION

1.1 Motivation

The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum based-fuels. Biodiesel, an alternative fuel, presents a suitable renewable substitute for petroleum base-fuel. This fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum diesel (Meher et al., 2006). It is usually produced by the tranesterification of vegetable oil or animal fat with short chain alcohol (Zullaiah et al., 2005). The reaction is commonly carried out in the presence of homogeneous alkali or acid catalysts. The alkali catalyzed process can achieve high purity and yield of biodiesel product in a short time but it is very sensitive to the purity of reactants, that is, the starting material (oil or fat) must be dried (moisture level <0.06%) and free of free fatty acid (FFA) (<0.5%). The presence of minor amount of FFA and moisture in the reaction mixture produces soap, which lower the yield of ester and renders the separation of ester and glycerol by water washing difficult. Moreover, FFA also consumed the catalyst and reduced catalyst efficiency (Zullaikah et al., 2005). The alternative is the acid catalyzed process, in which acid catalyst such as H_2SO_4 and HCl is used. Acid catalyzed process does have advantages such as reduced purification costs as no soap is produced and is therefore suitable for biodiesel production from oil with high FFA however the reaction is much slower than the alkali process (Mohamad et al., 2003; Zheng et al., 2006). A two-step transesterification process in which acid catalyzed process is followed by alkali catalyzed process has been developed to improve the yield of biodiesel for using oil with high FFA content (Wang et al., 2007). Although shorter reaction time is needed, no recovery of catalyst and high cost of reaction equipment were still the main disadvantages of this process.

In the homogeneous transesterification with liquid catalysts, recovery of the catalyst was not possible. Heterogeneous catalyst can therefore be used, nevertheless, there still appear to be some problems with this technique and finding a suitable

catalyst that is active, selective, and stable under the process conditions is the major challenge (Kiss et al., 2006). Alternatively, tranesterification using enzyme catalyst such as lipase can also convert oils and fats into methyl esters (Fukuda et al., 2001). Although the method is more environmentally friendly, the high cost of enzymes makes the process unattractive for industrial scale.

In the biodiesel industry, the price of feed stock was found to be one of the most significant factors affecting the economic viability of biodiesel manufacture (Zhang et al., 2003). It is reported that approximately 70–95 % of the total biodiesel production cost arises from the cost of raw material (Krawczyk et al., 1996). Therefore, inexpensive raw materials should be used to reduce the production cost. They contain high amounts of FFA. For Thailand, palm oil is the most suitable for production of biodiesel in the large scale due to its availability. Purified palm oil is however too expensive for the production to be economical feasible. Palm fatty acid, a by-product of palm oil refinery, on the other hand, is one of the most attractive raw materials due to its low cost. Furthermore, it is generally obtained in a purified form during the refining process of crude oil. Therefore palm fatty acid is a potential raw material for the production of biodiesel. Palm fatty acids cannot be directly processed into biodiesel by alkali catalyst, but can be catalyzed effectively by acid catalyst. Acid catalyzed esterification could be carried out in a single step, or two-step process, in which is acid catalyzed esterification of FFA with methanol is followed by alkali catalyzed process. The main disadvantage of the alkali or acid catalyzed homogeneous processes is the requirement of washing to eliminate the dissolved catalyst from the biodiesel product. This process causes a large amount of wastewater.

Alternative to the catalytic processes mentioned above, Saka and Kusdiana (2001) proposed a method of biodiesel production via non-catalytic transesterification of vegetable oils in supercritical methanol. In this process, the reaction takes place in a short time, as in the supercritical state, the reactants form homogeneous phase, which therefore eliminates diffusive problem. Furthermore, low cost feedstock (that with high free fatty acids content) could be used and the catalyst removal step is eliminated. However, some disadvantages of this method are the high temperature, high pressure and high methanol:oil ratio, which result in high energy consumption and high cost of production.

In order to reduce the above mentioned advantages, it is probable that addition of an appropriate solid catalyst which would allow the supercritical reaction

to be carried out under milder conditions. Demirbas (2007) investigated the transesterification reaction of sunflower oil in supercritical methanol with calcium oxide (CaO) which was found to considerably improve the transesterification reaction of sunflower oil. With 3 wt % CaO, the reaction was essentially completed within 6 min, at 525 K and 41:1 methanol/oil molar ratio. Several solid catalysts have been investigated for transesterification and esterification reactions (Furuta et al., 2004; Baba et al., 2005; Lo´pez et al., 2005; Kiss et al., 2006; Jitputti et al., 2006). Of these solid catalyst, sulfated zirconia (SO_4^{2-}/ZrO_2) have been shown to give high activity and selectivity for the transesterification and esterification of vegetable oils and fatty acids with a variety of alcohols (Lo´pez et al., 2005; Kiss et al., 2006; Jitputti et al., 2006). Although this catalyst is already of interest in several industrial processes, such as hydrocarbon isomerization, alkylation and esterification (Tanabe and Holderich, 1999), the study on the use of this catalyst for the production of biodiesel is limited. Thus, in this study, transesterification and esterification in supercritical methanol with SO_4^{2-}/ZrO_2 catalyst of purified palm oil and palm fatty acids was studied. The specific objectives are:

1.2 Objectives

1. To synthesize and characterize the SO_4^{2-}/ZrO_2 catalysts at different preparation condition.
2. To determine the suitable operating conditions for biodiesel produced from transesterification of purified palm oil and esterification of palm fatty acid in supercritical methanol with SO_4^{2-}/ZrO_2 catalysts.

1.3 Working scopes

1. To prepare SO_4^{2-}/ZrO_2 catalysts at different sulfur content and calcining temperatures.
2. To characterize the SO_4^{2-}/ZrO_2 catalysts prepared and compare them with that obtained commercially
3. To determine the effect of different catalysts prepared on the yield of biodiesel by transesterification of purified palm oil and by esterification of palm fatty acids.

4. To determine the effect of mass ratio of SO_4^{2-}/ZrO_2 catalysts to reactants (0-1 wt. %), reaction temperatures (200-300 °C), reaction time (0-15 min), molar ratio of methanol to purified palm oil (6:1-42:1) and methanol to palm fatty acid (3:1-12:1), on the biodiesel yield produced by transesterification of purified palm oil and esterification of palm fatty acid in supercritical methanol with SO_4^{2-}/ZrO_2 catalysts.
5. Determine the effect of recycling catalysts on the production of biodiesel in supercritical methanol with SO_4^{2-}/ZrO_2 catalysts.

1.4 Expected benefits

This investigation provides a process for the production of biodiesel from purified palm oil and palm fatty acids in which milder conditions are used by using supercritical methanolysis with SO_4^{2-}/ZrO_2 catalysts.