CHAPTER I

INTRODUCTION

As a renewable compound, glycerol has been traditionally produced as a by-product from biodiesel production process. Biodiesel is recognized as an ideal alternative diesel fuel due to its environmental benefits and its origin from renewable resources including vegetable oils or animal fats. Most biodiesel is currently produced by transesterification of triglycerides with methanol. For every 9 kg of biodiesel produced, about 1 kg of glycerol is formed as a by-product. With the escalating production and use of biodiesel worldwide, glycerol becomes more readily available with descending price. This has promoted intensive searches for novel technologies to convert glycerol to value-added chemicals like propylene glycol.

Propylene glycol also called 1,2 propanediol, is an important specialty chemical with many applications. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, paint and animal feed. At present, propylene glycol is mainly produced from petroleum-derived propylene or ethylene via process involving selective oxidation and subsequent hydration; these methods are restricted by the supply of olefins due to the dwindling and unstable supply of petroleum. Extensive research efforts have been devoted to developing Bio or chemical synthesizing processes using renewable substitutes as feed. In this respect, glycerol has emerged as a promising candidate. Although many different processes have been studied, the catalytic dehydroxylation of glycerol to propylene glycol seems to be a highly promising alternative route.

The catalytic dehydroxylation of glycerol to propylene glycol can be carried out in the presence of metallic catalysts and hydrogen. A previous study (Sitthisa, 2007) has demonstrated the effectiveness of Cu/Al_2O_3 catalyst. The results showed that 100% glycerol conversion and 90% propylene glycol selectivity were obtained. However, the conversion decreased drastically after 6 h. Swangkotchakorn (2008) introduced ZnO into Cu/Al_2O_3 catalyst and found that the addition of ZnO could prolong the stability of the catalyst. Chirddilok (2009) found that the $CuZnO/Al_2O_3$ catalyst showed superior catalytic activity to Cu/Al_2O_3 and Cu/ZnO catalysts. Panyad

(2011) concluded that the $CuZnO/Al_2O_3$ catalyst prepared by the IWI method exhibited the highest catalytic activity and stability as compared to the ones prepared by the SG and COP methods. The causes of catalyst deactivation were the combination of coke formation and sintering of active copper metals. Auttanat (2012) reported that the catalytic dehydroxylation of glycerol to propylene glycol using $CuZnO/Al_2O_3$ catalyst and refined glycerol as feedstock gave the higher catalytic activity than technical grade glycerol. The ICP-EOS results indicated that the catalyst deactivation caused by the deposition of alkaline contaminated in the feedstocks. The higher amount of impurity (especially Na and K) resulted in the lower catalytic activity. Wongpraphairoat (2013) studied the catalytic conversion of glycerol to propylene glycol over CuZnO–based catalysts with different catalyst supports ($CuZnO/Al_2O_3$, CuZnO/MgO, CuZnO/HT, CuZnO/ASA.) and found that CuZnO/MgO exhibited the highest performance in terms of stability. The regenerated CuZnO/MgO gave the glycerol conversion as good as the fresh catalyst.

In the present study, the catalytic dehydroxylation of glycerol to propylene glycol will be conducted over the CuZnO catalyst supported on MgO prepared by two different methods–incipient wetness impregnation (IWI) and co-precipitation (COP). The main purpose was to investigate the effect of catalyst preparation with an intention to improve the conversion of glycerol and selectivity of propylene glycol. Moreover, the catalyst regeneration and deactivation were investigated.