CHAPTER I
INTRODUCTION

There has been a considerable interest in developing biodiesel as an alternative fuel in recent years because it is a renewable fuel that is non-toxic, biodegradable and environmentally friendly. For every 9 kilograms of biodiesel produced, about 1 kilogram of a crude glycerol by-product is formed (Dasari *et al.*, 2005). As the biodiesel production is increasing, the crude glycerol is also produced in a large quantity.

Since the crude glycerol obtained from biodiesel production contains residual catalysts, water and other organic impurities, most of the larger biodiesel producers purify and refine this crude glycerol by several steps including vacuum distillation for the wide applications in food, pharmaceutical, cosmetics, and many other industries. It is too costly to refine the crude glycerol to a high purity so, many smaller plants simply discard the glycerol by-product as a waste (Chiu *et al.*, 2006).

Nowadays, with plenty of glycerol available to the world markets, prices of glycerol will continue to drop with an oversaturated market. Thus, an effective usage or conversion of crude glycerol to other commodity chemicals which cut down the biodiesel production costs is desirable.

One of the most attractive routes is the catalytic dehydroxylation of glycerol to propanediols. Propanediols may refer to either of two isomeric organic chemical compounds: 1,2-propanediol (propylene glycol) and 1,3-propanediol. Propylene glycol is a major commodity chemical used in the production of unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors and fragrances, personal care, paints and animal feed. 1,3-Propanediol is mainly used in polyester fibers, films, adhesives, laminates, mouldings, solvents, and coatings. In the market, the price of 1,3-propanediol is generally higher than that of propylene glycol; however, the use of the former is much greater. These considerations led us to focus on the production of propylene glycol for which such a technology could also be used in biodiesel production plants to increase profitability.

The catalytic dehydroxylation of glycerol to propanediol 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 $Cu\text{-}ZnO/Al_2O_3$ catalyst showed the best catalytic activity compared with Cu/Al_2O_3 and Cu/ZnO catalysts. The maximum activity was obtained from the catalyst prepared by co-precipitation as compared with incipient wetness impregnation.

In the present work, the catalytic dehydroxylation of glycerol to propylene glycol will be conducted over the $Cu\text{-}ZnO/Al_2O_3$ catalyst prepared by sol-gel method. The main purpose is to investigate the effects of catalyst preparation conditions with the intention to improve the conversion rate of glycerol and selectivity towards propylene glycol. This study deals with the effects of preparation methods on the catalytic performance of the $Cu\text{-}ZnO/Al_2O_3$ catalysts in the dehydroxylation of glycerol. The performance and stability of the $Cu\text{-}ZnO/Al_2O_3$ catalyst prepared by sol–gel method will be compared with those of previously investigated ones, incipient wetness impregnation and co-precipitation. In addition, the catalyst regeneration and deactivation were studied.