CHAPTER I
INTRODUCTION

Glycerol is an inevitable by-product from transesterification of triglyceride in biodiesel production. Since utilization of biodiesel dramatically increases, glycerol will be significantly over-supplied, resulting in lower its value. Therefore, to help the overall economics of biodiesel, it is expected to increase the use of glycerol and its value by converting to higher value products.

Glycerol can be found in many applications, for example, in pharmaceuticals, toothpaste, cosmetics, tobacco, foods, and urethanes. It also is used as a feedstock for the production of various chemicals. Propylene glycol can be converted from glycerol for use in foods, pharmaceuticals, cosmetics, liquid detergents, and antifreeze. Glycerol can be dehydrated to acrolein which is an important bulk chemical used as a feedstock for acrylic acid production, pharmaceuticals, fiber treatments, and herbicide. Furthermore, glycerol has also been considered as a feedstock for new industrial fermentations in the future.

Among its applications, glycerol could be used as a starting material for the synthesis of polyglycerol which is used directly or esterified with fatty acid for use as an emulsifier in the cosmetics and food industry. Products based on polyglycerols are useful in surface-active agents, plasticizers, adhesives, lubricants, antimicrobial agents, medical specialties, and dietetic foods.

The polymerization of glycerol requires high temperature and alkaline condition which a mixture of polyglycerols is obtained. Because of the variety of the products, it is difficult to control their hydrophilic–lipophilic balance after esterification, biodegrability, performances and environmental impact. Therefore, low amounts of catalyst and short reaction times are required to control the polymerization and to obtain compositions with a low polymerization degree.

Generally, the preparation of diglycerol which is the simplest polyglycerol can be carried out in the presence of homogeneous base catalysts, such as Na_2CO_3. The catalyst can increase the rate of reaction and the products containing diglycerol, triglycerol, higher degree of glycerol oligomers. However, there are several disadvantages from using homogeneous catalysts, for example, product selectivity and the downstreams catalysts separation. Moreover, the product is often required further processes to separate impurities and catalysts. The use of heterogeneous or solid catalysts can possibly avoid these drawbacks. The use of solid catalysts have several advantages such as ease of catalysts and products separation, reuse and recycle which result in lower production cost and safer environments.

Various types of solid base catalyst have been tested. Zeolites which have high-alumina provide good selectivity toward linear di- and triglycerols at 513 K. Moreover, the studies also have been extended to other zeolites and mesoporous molecular sieve materials containing La, alkalines, or alkaline earths. However, the main problem with these catalysts is the leaching of metals.

In this work, glycerol etherification catalyzed by alkaline earth oxides was studied. Barium oxide (BaO), calcium oxide (CaO), and magnesium oxide (MgO) were selected for use as potential heterogeneous catalysts which give high activity, reduce metal leaching concern, and have many commercial advantages. Parameters such as types of catalyst, reaction time and reaction temperature were examined. Moreover, the kinetics of the etherification to diglycerol was determined. Based on the kinetics data, a 20-kilogram pilot scale batch reactor was designed and constructed for testing the operating conditions.