

CHAPTER I

INTRODUCTION

1.1 General Introduction

The partial oxidation of ethylene, so-called ethylene epoxidation has been increasingly important for petrochemical industry because this chemical reaction produces ethylene oxide (C_2H_4O , EO) used as a key feedstock or intermediate for the production of various useful chemicals. Ethylene glycol, almost 60% converted from EO, is used to produce polyesters and also used as an anti-freeze reagent and an automotive coolant. In addition, it is an important precursor to produce surfactants by ethoxylation processes, and it is also employed as a sterilant for foodstuffs, in medical equipment and supplies, and as a fumigant in agricultural products (ATSDR, 1990). Therefore, this epoxidation reaction has been investigated extensively.

Generally, silver-based catalysts, especially low-surface-area α -alumina-supported silver catalysts ($Ag/(LSA) \alpha-Al_2O_3$) are commercially used for ethylene epoxidation. Alkali and transition noble metals, especially Cs, Cu, Re, and Au, as well as halogen promoters such as Cl, have been proved to increase the efficiency of the catalytic process in a term of enhancement of EO selectivity (Campbell and Paffett, 1984; Campbell, 1986; Dellamorte *et al.*, 2007; Jankowiak and Barteau, 2005; Jun *et al.*, 1992; Kapran, and Orlik, 2005; Macleod *et al.*, 2003; Marta *et al.*, 2007; Rafael *et al.*, 1990; Tan *et al.*, 1987; Torres *et al.*, 2008). However, the currently-used catalytic processes require high temperatures for efficient operation, resulting in high energy consumption. In addition, catalyst deactivation results from both coke formation and sintering of active sites on the catalyst surface commonly occurs at high temperatures, leading to decreases in both catalytic activity and desired product selectivity. Therefore, new techniques and further catalyst development are required to solve these limitations and to increase efficiency of the epoxidation process.

Non-thermal plasma is a promising technique for many potential applications, such as surface modification (Kim *et al.*, 2007), chemical synthesis (Thevenet *et al.*, 2010; Torres *et al.*, 2008; Yu and Chang, 2001), hydrocarbon reforming (Heintze and

Pietruszka, 2004; Li *et al.*, 2010), and gas treatment (Durme *et al.*, 2008; Rosacha *et al.*, 1993). An interesting characteristic of the non-thermal plasma is that the bulk gas temperature is still very low (close to ambient temperature) while generated high energy electrons have a much higher temperature (approximately 10^4 - 10^5 K) (Rosacha *et al.*, 1993; Suhr *et al.*, 1984). As a consequence, the non-thermal plasma can be operated at an ambient temperature and atmospheric pressure, leading to low energy consumption. Hence, catalyst deactivation under high-temperature operation can also be avoided by this technique. The plasma discharges can be generated by applying an electrical current with a sufficient voltage across metal electrodes. Subsequently, the reactant gases passing through the plasma discharge zone are collided with the generated electrons to create various high energetic species, leading to initiation of subsequent chemical reactions.

There are several types of non-thermal plasmas, i.e. dielectric barrier discharge, corona discharge, glow discharge, microwave discharge, and radio frequency discharge. Dielectric barrier discharge (DBD) is one of the most effective techniques and has been widely used in various applications (Eliasson *et al.*, 1987; Kim *et al.*, 2007; Sreethawong, *et al.*, 2008; Thevenet *et al.*, 2010; Quoc Ana *et al.*, 2011; Yu and Chang, 2001). A main advantage of DBD is that it can produce fairly uniform plasma distribution over the entire electrode surface, resulting in the high efficiency for chemical reactions. The corona discharge is also used in the industrial applications (Bröer and Hammer, 2000; Chang *et al.*, 1991; Chavadej *et al.*, 2008; Yan *et al.*, 1998; Zhang *et al.*, 2010) because it is capable of combining with heterogeneous catalyst and operating at low temperature and atmospheric pressure, as well as it is easy to construct. In this research, both DBD and corona systems were used for ethylene epoxidation.

Because of the advantages of both catalytic processes—providing the active site to catalyzed the chemical reaction—and plasma systems—ambient temperature and atmospheric pressure operation, many research studies have attempted to combine a catalyst with a plasma system for improving the activity of chemical reaction. Therefore, the ethylene epoxidation over supported silver catalysts was studied in a parallel plate DBD system (Chapter IV).

However, the further development of a plasma technique has been great of interest for several chemical reactions (Chavadej *et al.*, 2008; Durme *et al.*, 2008; Heintze and Pietruszka, 2004; Liu *et al.*, 1997; Malik, 1999). Generally, ethylene (C_2H_4), oxygen (O_2), and helium (He, as a balance gas) are basically fed into a plasma reactor as the mixed feed for ethylene epoxidation reaction. Hence, both C_2H_4 and O_2 molecules are collided by the energetic electrons to initiate several subsequential chemical reactions including ethylene epoxidation and undesired reactions. It was hypothesized that a separate feed of C_2H_4 from O_2 with a suitable C_2H_4 feed position could reduce all the mentioned undesired reactions including cracking, dehydrogenation, coupling, and complete oxidation reactions of C_2H_4 , resulting in a higher EO selectivity and lower by-product selectivities. Hence, the separate C_2H_4/O_2 feed system was employed in a cylindrical DBD (Chapter V) and a corona discharge reactor (Chapter VI). In addition, various operational parameters were also investigated in order to determine the best conditions.

Atmospheric plasma jets— dielectric barrier discharge (DBD) jets— have currently been great of interest in current low-temperature plasma research (Lei and Fang, 2011). The plasma jet reactors can generate highly reactive chemical species by using gas stream to blow the plasma out of its production region, thus it is convenient to operate and be employed in practical applications such as surface modification, thin-film deposition, and biomedicine [Chiang *et al.*, 2010; Guimin *et al.*, 2009; Merche *et al.*, 2009; Panousis *et al.*, 2007; Pulpytel *et al.*, 2011, Shao *et al.*, 2011). In addition, the plasma jet was investigated in the epoxidation of 1-decene to produce the epoxy products (Yoshinori and Hidetoshi, 2006). It was hypothesized that a plasma jet could provide a better improvement for ethylene epoxidation performance. Therefore, a new designed DBD jet for ethylene epoxidation was study in Chapter VII.

1.2 Objectives

The main objective was to study the ethylene epoxidation in low-temperature plasma systems with and without supported silver catalysts and this work was divided into four parts as follows:

1. to study the combination of silver catalysts loaded on two different supports (SiO_2 and Al_2O_3 particles) in a low-temperature DBD system for ethylene epoxidation reaction,
2. to study the effects of the separate $\text{C}_2\text{H}_4/\text{O}_2$ feed and other operating conditions, i.e. $\text{O}_2/\text{C}_2\text{H}_4$ feed molar ratio, applied voltage, input frequency, and total feed flow rate, on the ethylene epoxidation in a cylindrical DBD system,
3. to study the effects of distance between plate electrode and C_2H_4 feed position and other operating conditions on the ethylene epoxidation under a low-temperature corona discharge system, and
4. to study the effects of total feed flow rate, oxygen-to-ethylene feed molar ratio, applied voltage, input frequency, and inner electrode position on the ethylene epoxidation in a low-temperature DBD jet system.

1.3 Scope of Work

In this work, the ethylene epoxidation reaction was investigated in four different non-thermal plasma reactors: a parallel plate DBD, cylindrical DBD, corona discharge, and DBD jet. In the first part (Chapter IV), silver catalysts supported on alumina (Al_2O_3) and silica (SiO_2) particles were applied in a parallel plate DBD system for improving the ethylene epoxidation. The combination of catalytic and plasma behaviors was studied in terms of C_2H_4 and O_2 conversions, EO selectivity and yield, selectivities for other products, and power consumption. In addition, several possible chemical pathways were comparatively proposed between the sole DBD system and the combined catalytic and plasma system, based on the experimental results. For a second part (Chapter V), O_2 balanced with helium was initially fed into a cylindrical DBD reactor while C_2H_4 was directly injected to the plasma zone at different locations along the length of the reactor's electrode, so-

called the separate C_2H_4/O_2 feed. The comparative results between the separate C_2H_4/O_2 feed and the mixed feed as well as the significant role of operating process parameters on the plasma reactions were discussed. For the third part in Chapter VI, a corona discharge reactor with the separate feed was investigated for ethylene epoxidation. The effects of the distance between plate electrode and C_2H_4 feed position and operating process parameters, including O_2/C_2H_4 feed molar ratio, applied voltage, input frequency, total feed flow rate, and gap distance between pin and plate electrodes, on the plasma performance were analyzed in order to find out the optimum conditions. In the final part (Chapter VII), the corona discharge reactor was modified to be a DBD jet reactor in order to obtain both advantages of corona discharge and cylindrical DBD systems. A high flow rate of argon was used as a balancing gas to extend the plasma length in order to enhance the plasma efficiency. The effects of total feed flow rate, oxygen-to-ethylene feed molar ratio, applied voltage, input frequency, and inner electrode position on the ethylene epoxidation were investigated.