# Chapter 1

# Introduction

For production of olefins from paraffins, such as cracking ethane to ethylene, the process must be carried out at temperature about 1070-1270 K with a residence time in the order of millisecond in order to obtain desired conversion of ethane. Afterwords, the effluent consisting of ethylene and small amount of hydrogen, methane, ethane and acetylene must be quenched to stop all reactions and to separate the mixture with a conventional cryogenic distillation. Thereafter, pure ethylene from the distillation unit must be heated to the temperature about 320-430 K for polymerization, as illustrated in Figure 1.1. In such a process, the temperature integration is so large that the integrated energy is rarely efficient. Therefore, other separation technologies ought to be exploited.

An adsorption process is an alternative for the direct separation of the mixture in gas phase. The operation may depend on at least one of the components of the gas mixture being adsorbed more strongly than the others at equilibrium or being adsorbed faster than the others [1]. With adsorption of by product from

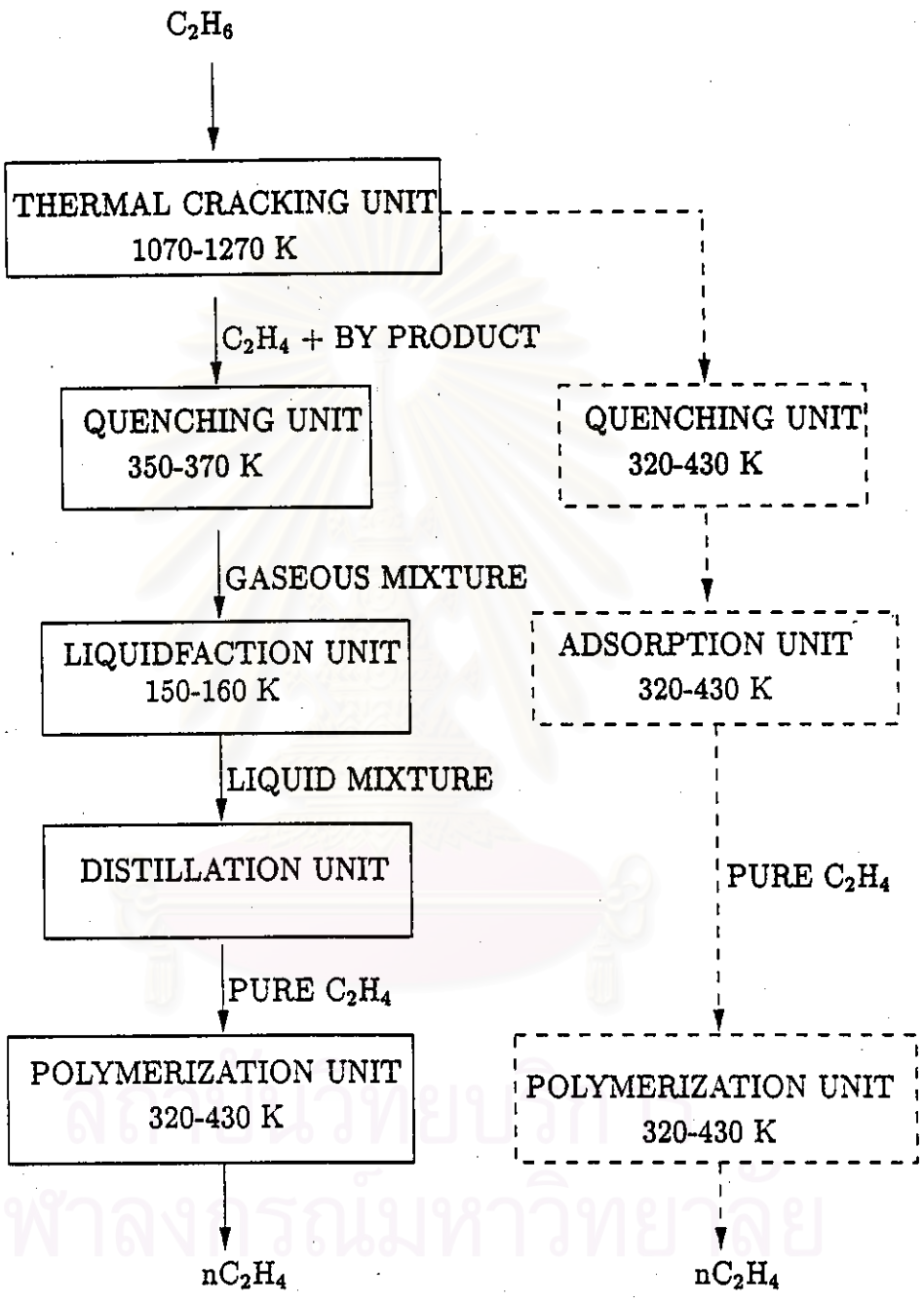


Figure 1.1: The alternative adsorption process for selective removal of by product from ethane cracking

ethane cracking, pure ethylene is obtained with lower temperature integration compared with the conventional distillation scheme, as illustrated by the dash line in Figure 1.1.

Since numerous materials can be used as adsorbents and many novel concepts for processing adsorption system are generated, the efficiency of adsorption can be improved by selecting an appropriate adsorbent and a suitable mode of operation. Although an abundance of adsorbents, such as activated carbons, silica gel, activated alumina and zeolite molecular sieves, have been used widely in separation processes, only activated carbons and zeolites with high Si/Al ratio have been considered in many hydrocarbon separation researches according to their nonpolar or slightly nonpolar property [2, 3, 4, 5, 6].

The fundamental requirement for the design of adsorption system used for separation of gas mixtures is the information regarding adsorption isotherms and kinetics of the system. Both parameters are the important criteria for selection of a suitable adsorbent. Adsorption isotherm data can be easily obtained by direct measurement of the amounts of adsorbed component in both gas and adsorbed phases after achievement of the equilibrium. On the other hand, accurate kinetic data including mass transfer rate parameters are more difficult to obtained [7]. Therefore, an abundance of the adsorption isotherm data exist in the literature whereas relatively little experimental mass transfer data have been reported. P. Schneider and J.M. Smith (1968) [8] determined the adsorption equilibrium con-

stants, rate constants and intraparticle diffusivites for the adsorption of ethane, propane and n-butane on silica gel by the use of chromatographic technique. T. Victor Lee and Jan Chang Huang (1984) [2] investigated the adsorption isotherm of pure ethane, pure acetylene and of each gas in the mixtures on columbia 4 LXC 12/28 activated carbon by the use of gas chromatograph. Thereafter, T. Victor Lee continued in his work, incorporating Richard Madey (1985) [3] measured the adsorption isotherms for pure propane and for the mixture of ethane and propane on the corresponding activated carbons. A. Gorius and M. Bailly (1991) [9] presented a new theoretical approach for determining mass transfer coefficient by the use of non-linear chromatography, based on perturbation analysis. A simple method for the estimation of an adsorption isotherms based on the analysis of an experimental desorption curve was studied by Kanji Miyabe and Motoyuki Suzuki (1991) [10]. This methods taking into account the effects of mass transfer rate. More recently, A. Malek and S. Farooq (1996) [11] proposed two excellent methods for obtaining single-component adsorption isotherm data, i.e. the dynamic column breakthrough (DCBT) method and the constant flow equilibrium desorption (CFED) method. Both methods were used to derive the adsorption isotherms of methane, ethane and propane in on activated carbons and silica gels.

In addition to the information reguarding adsorption isotherms and kinetics, the variation of concentrations of an adsorbed component in an adsorber provide information for the rational design of an adsorber. These profiles can be

determined from the experimental breakthrough characteristic of the system. The variation of the profile depends upon axial dispersion, the shape of adsorption equilibrium or isotherm and rate of adsorption. A large fraction of adsorption systems involves favorable isotherm, in which the slope of the isotherm decrease with an incresase in concentration [12]. In these cases, the profile spreads as it propagates initially, due to the effects of the mass transfer rate and the axial dispersion. At some distance from the entrance, it reachs a constant pattern condition and thereafter it propagates with no further change in shape [13]. The information regarding the concentration profile under constant pattern condition provides the basis of a simple design method which permits reliable scale-up from small-scale laboratory experiments.

Although a number of model for predicting the breakthrough characteristic under constant pattern condition have been proposed by many investigator, relatively little experimental data have been reported, due to the physical complexity. Cooney and Lightfoot (1965) [14] proved the existence of a constant pattern condition for single and multicomponent adsorption and Cooney and Strusi (1972) [14] obtained analytical solutions for the concentration profile of two solutes under a constant pattern condition. Miura et al.(1979) [14] suggested a method for determining breakthrough characteristics of bicomponent fix-bed adsorption under a constant pattern and linear driving force. The new approximate analytical expression for constant pattern profile were reported by A. Gorious and M. Bailly

(1990) [15]. They also shown how these profiles depend on the kinetic mechanism. More recently, Jack S. Watson (1995) [12] simplified a prediction method of breakthrough characteristic for constant pattern adsorption and ion exchange.

In addition, the minimum distance required to approach constant pattern limit depends on the operating conditions of the system. Therefore, it is essential to analyse the effect of experimental conditions on the dynamic behavior of the system. F. Foeth and M. Andersson (1994) [4] determined the effects of temperature, feed concentration and superficial velocity on the breakthrough characteristic of dilute gas mixtures containing carbon dioxide and methane on Norit RB1 activated carbon. Kye Soon Huang and Wan Kook Lee (1994) [14] investigated the effect of the total pressure and the feed concentration on the breakthrough characteristic of carbon dioxide and carbon monoxide on Norit B4 activated carbon. J.J. Perona and A.C. Coroneos (1995) [16] proposed a simple model for strontium breakthrough on zeolite columns and studied the effects of superficial velocity on the length of mass transfer zone. More recently, F. Foeth and H. Bosch (1996) [17] determined the breakthrough characteristic of Pressure Swing Adsorption (PSA) process with variable superficial velocity and pressure.

The main objective of this work is to investigate the effects of bed lengths, superficial velocity , feed concentration and adsorbent sizes on the concentration profile. Another objective is to determine the adsorption isotherm and mass transfer coefficient for the adsorption system.