CHAPTER I

INTRODUCTION

I.1. Background

Organic carboxylic esters are compounds that are formed by a condensation reaction between a molecule of carboxylic acid and a molecule of alcohol or phenol with elimination of water as depicted in the following equation.

$$R^1COOH + R^2OH \rightleftharpoons R^1COOR^2 + H_2O$$

The names of esters consist of two words that reflect their formation from an alcohol and a carboxylic acid. According to the IUPAC rule, the alkyl or aryl group of the alcohol is cited first followed by the carboxylate group of the acid with the ending "-ate" replacing the "-ic" of the acid. For example, $CH_3CH_2COOCH_3$, the methyl ester of propanoic acid is called methyl propanoate [CAS 554-12-1] (or methyl propionate, if the trivial name, propionic acid, is for the carboxylic acid). The monoesters of dibasic acids are named by inserting the word hydrogen between names of the alcohol and the carboxylate. The monomethyl ester of succinic acid, $CH_3OCOCH_2CH_2COOH$, is called methyl hydrogen succinate or more systematically methyl hydrogen butanedioate [CAS 3878-55-5]. In fully esterified polybasic acids, the names of alkyl or aryl groups are cited in alphabetical order, eg, Ethyl methyl malonate.

Currently, most of the simple esters used commercially are of synthetic origin, although esters occur naturally in large quantities in oils, fats, and waxes. Oils and fats from plants and animals consist mainly of glycerol esters of stearic, palmitic, and oleic acids. Synthetic esters are generally prepared by reaction of an alcohol with an organic acid in the presence of a catalyst such as sulfuric acid, p-toluenesulfonic acid, or ion-exchange resins of the sulfonic acid type. The reaction, known as the Fischer esterification, is a simple route to esters from readily available starting materials. Equilibrium constants for esterification are often relatively small in magnitude.

Ethyl acetate is used primarily as a solvent for various resins in protective coatings; it is also used extensively in formulating printing inks and adhesives; new applications include its uses as a process solvent in the pharmaceutical industry and as an extraction solvent in food processing; as a substitute for methyl ethyl ketone (MEK) in many applications [Kirk-Othmer, 1978].

In Indonesia the only company that produces ethyl acetate is PT. Sarasa Nugraha, Tbk. with production capacity of 4,500 tons/year. On the other hand, the demand of ethyl acetate is growing each year. To fulfill the increasing demand of ethyl acetate, Indonesia still imports every year, and the amount of imported ethyl acetate also increases as the demand. Therefore, the existance of another ethyl acetate producing company is plausible.

I.2. Raw Materials and Product

In chemical industrial process, it is important to understand the raw materials and product specifications in order to set the best operating conditions during the whole manufacture process. In this ethyl acetate production plant, the raw materials used are ethanol and acetic acid with PTSA (Paratoluene Sulfonic

Acid) as the catalyst. The product is designed to have 99.5% w/w purity. The specifications of raw materials and product are given in the following subsections.

I.2.1. Ethanol

Ethanol used in this production is obtained from several suppliers; some of them are as follows,

- PT. Molindo Raya Industrial, Lawang, Malang
- PT. United Chemicals, SIER, Surabaya
- PT. Adiguna Eka Sejahtera, Buduran, Sidoarjo
- PT. Karsavicta Satya, Jakarta

Ethanol with low water content (95% v/v of ethanol) is used because the Fischer esterification method is reversible, thus more water available will drive the reaction towards ester deformation.

The physical properties of ethanol are as follows,

- **Appearance:** Clear, colorless liquid.
- **Odor:** Mild pleasant whiskey-like odor.
- **Solubility:** Miscible in water.
- **Density:** 0.79 at 20°C/4°C
- **pH:** No information found.
- **% Volatiles by volume at 21°C (70°F):** 100
- **Boiling Point:** 78°C (172°F) (ethanol)
- **Melting Point:** -114°C (-173°F) (ethanol)
- **Vapor Density (Air=1):** 1.6 (ethanol)

- **Vapor Pressure (mm Hg):** 40 at 19°C (66°F)
- **Evaporation Rate (BuAc=1):** ca. 1.4 (CCl_4=1)

I.2.2. Acetic Acid

Acetic acid used in this production is obtained from several suppliers; some of them are as follows,

- PT. Aneka Kimia Inti, Graha S.A., Gubeng, Surabaya
- PT. Bumi Prima Lestari, Margomulyo, Surabaya
- PT. Indokemika Jayatama, Margomulyo, Surabaya
- PT. Pintu Mas Mulya Kimia, Margomulyo, Surabaya
- PT. Mulya Adhi Paramita, Cilegon, Banten

The acetic acid used is pure acetic acid, since it is widely available and will drive the reaction into completion.

The physical properties of acetic acid are as follows,

- **Molecular Weight:** 60.05
- **Chemical Formula:** CH_3COOH
- **Appearance:** Clear, colorless liquid.
- **Odor:** Strong, vinegar-like.
- **Solubility:** Infinitely soluble.
- **Density:** 1.05
- **pH:** 2.4 (1.0M solution)
- **% Volatiles by volume at 21°C (70°F):** 100
- **Boiling Point:** 118°C (244°F)

- **Melting Point:** 16.6°C (63°F)
- **Vapor Density (Air=1):** 2.1
- **Vapor Pressure (mm Hg):** 11 at 20°C (68F)
- **Evaporation Rate (BuAc=1):** 0.97

I.2.3. Paratoluene Sulfonic Acid (PTSA)

In this particular reaction, PTSA acts as an acid catalyst. In previous processes usually used in the ethyl acetate industry, the catalyst used is commonly sulfuric acid, but the main drawback of this catalyst is that it requires further separation process to separate the catalyst from the products formed since they are of the same phase. The reason of choosing PTSA as catalyst is because it remains in solid state during the course of the reaction. Thus, the separation processes needed will be simpler, since the catalyst can be held using fixed bed in the reactor.

The physical properties of PTSA is given as follows,

- **Molecular Weight:** 190.22
- **Chemical Formula:** $C_7H_8O_3S.H_2O$
- **Appearance:** Off-white crystals.
- **Odor:** Odorless when pure; technical grade has a slight aromatic odor
- **Solubility:** 67g/100mL water, anhydrous.
- **Density:** 1.23-1.24 g/cm^3 at 20°C (anhydrous)
- **pH:** No information found.
- **% Volatiles by volume at 21°C (70°F):** No information found.

- **Boiling Point:** 140°C (284°F) at 20mm , anhydrous
- **Melting Point:** 103 - 106°C (217 - 223°F)
- **Vapor Density (Air=1):** 6.0
- **Vapor Pressure (mm Hg):** No information found.
- **Evaporation Rate (BuAc=1):** No information found.

I.2.4. Ethyl Acetate

Ethyl acetate produced from the process is of 99.5% w/w purity. The physical properties of ethyl acetate are as follows,

- **Molecular Weight: 88**
- **Chemical Formula:** $CH_3COOC_2H_5$
- **Appearance:** Clear liquid.
- **Odor:** Fruity odor.
- **Solubility:** 1 ml/10ml water at 25°C
- **Specific Gravity:** 0.902 at 20°C/4°C
- **pH:** No information found.
- **% Volatiles by volume at 21°C (70°F):** 100
- **Boiling Point:** 77°C (171°F)
- **Melting Point:** -83°C (-117°F)
- **Vapor Density (Air=1):** 3.0
- **Vapor Pressure (mm Hg):** 76 at 20°C (68°F)
- **Evaporation Rate (BuAc=1):** 6

I.3. Capacity Selection

In Indonesia the only company that produces ethyl acetate is PT. Sarasa Nugraha, Tbk. On the other hand, the demand of ethyl acetate are increasing as shown in the following table.

Table I. 1. Data of ethyl acetate production, import, and export in Indonesia (in kg) [BPS, 2000-2005]

Year	Production	Import	Export	Demand
2000	4,576,044			
2001	5,069,615	14,271,451	11,862,336	7,478,730
2002	4,156,010	17,673,540	7,075,631	14,753,919
2003	3,204,912	18,782,643	3,528,154	18,459,401
2004	3,205,676	19,636,585	3,025,323	19,816,938
2005		20,215,285	5,677,926	

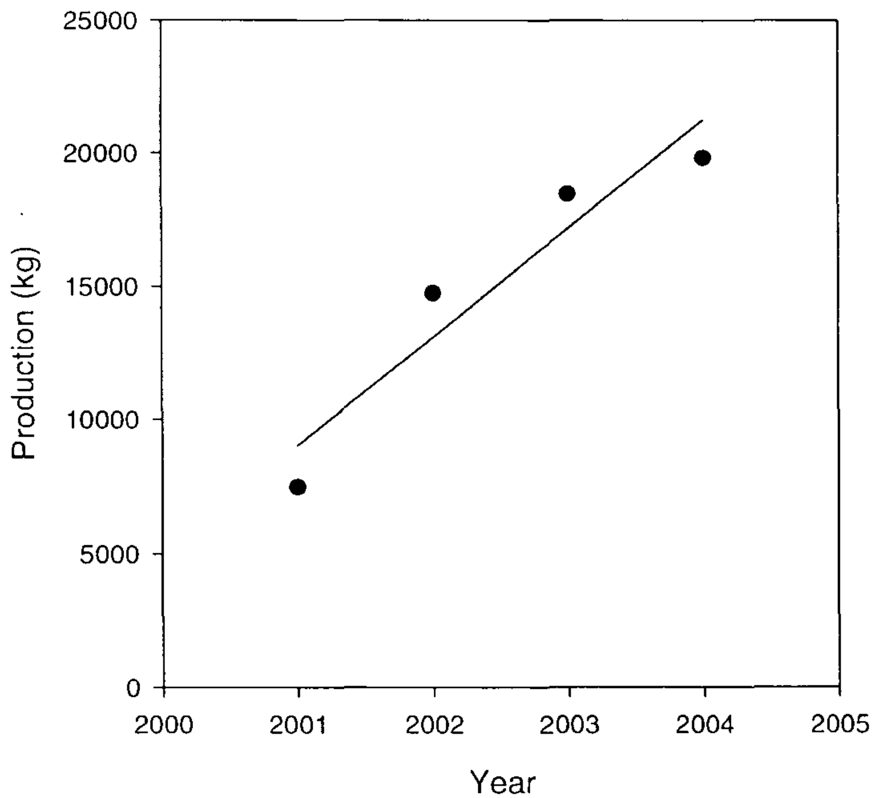

Figure I. 1. Demand of ethyl acetate in Indonesia

Based on Figure I. 1., the linearization gives the following equation,

$$y\,(\text{demand}) = -8.139 \cdot 10^{6} + 4.072 \cdot 10^{3} \cdot x\,(\text{year})$$

It is calculated that in 2010, the demand will reach approximately 46,000 tons/year. Since the construction of the plant will take approximately three years to completion, the capacity of the plant is designed to fulfill 30% of the projected demand, which is approximately 14,700 tons/year.

Another consideration to specify the production capacity is the raw materials availability. The following table shows the production of ethanol and acetic acid in Indonesia.

Table I. 2. Data of ethanol and acetic acid production in Indonesia [BPS, 2000-2004]

Year	2000	2001	2002	2003	2004
Ethanol (kL)	11,870	40,354	41,416	51,710	53,429
Acetic acid (tons)	15,776	10,367	19,337	21,369	24,771

Based on the designed production capacity of 14,700 tons ethyl acetate/year; the ethanol needed is approximately 12,800 kL/year, while the acetic acid needed is approximately 10,800 tons/year. Consulting Table I. 2, it can be seen that the local ethanol and acetic acid production is sufficient to fulfill the plant's demand. Considering the demand growth and raw materials availabilty, the recommended ethyl acetate production capacity is reasonable.

Other industries that use the same raw materials are fuel, beverage, and toiletries industries that use ethanol as their raw material, while textile, pharmaceuticals, and vinyl acetate industries use acetic acid as their raw material. In case of the raw materials supply from the local market could not fulfill the plant's demand; the company will import the chemicals, either from China or other neighboring countries.

Besides producing pure ethyl acetate, the plant also produces side product of ethyl acetate of 48 % purity. This side product will be sold to industries that could use ethyl acetate of this grade such as the varnish, paint, printing inks, perfumes, wood furniture coating, and automobile refinishing industries. By doing so, the efficiency of the plant could be maximized.