SIMULATION: OPTIMIZE THE PRODUCTION OF BENZOIC ACID BY USING BENZENE AND ACETIC ANHYDRIDE

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A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"SIMULATION: OPTIMIZE THE PRODUCTON OF BENZOIC ACID BY USING BENZENE AND ACETIC ANHYDRIDE"** was prepared by **CHIN KAH LOONG** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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Date : _________________________

Specially dedicated to
my beloved mother and father

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ABSTRACT

Benzoic acid production from oxidation of toluene is widely used in the industry. This study is to develop a new process that applied green technology to replace the current benzoic acid production process. The idea of this project was to introduce heterogeneous catalyst to replace the homogenous catalyst in the acylation of benzene by acetic anhydride due to the economic and environment factors. On the other hands, replacement of potassium permanganate (IV) by sodium hypochlorite in the oxidation process to produce benzoic acid was recommended because of the cheaper cost and less hazardous. Another purpose of this study was to identify the effect of various operating parameters such as reaction temperature and material molar flow rate to get the optimum benzoic acid production. The process of benzoic acid production was successfully simulated by using ASPEN HYSYS 3.2. In this study, benzene and acetic anhydride was chosen as starting materials. The benzoic acid production plant in this study consist of packed bed reactor, two distillation column, four heat exchangers, two conversion reactors, two separators and two hydro cyclones. Besides, economic analysis of benzoic acid production is studied in this study to estimate the net profit value. From the results, the benzoic acid purity obtained in the process is 89% and the payback period is estimated within 3 years. Net profit is estimated to be US$ 890.6/MT or US$ 33 million per year.

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LIST OF SYMBOLS / ABBREVIATIONS

C_{BM}	bare module cost
c_p	specific heat capacity, J/(kg·K)
C_P	purchase cost
D_i	Internal diameter, ft
D_o	Outer diameter, ft
E_T	separation efficiency
F_{BM}	bare module factor
F_M	material factor
F_P	pressure factor
H	height, ft
ΔH^{o}_{Rx}	heat of reaction
L	length, ft
M	mass flow rate, kg/s
N_m	number of independent variables
N_{om}	number of manipulated variables with no steady state effect
N_{oy}	number of variables that need to be controlled from N_m
N_{ss}	number of variables needed to be specified
P	pressure, kPa
P_b	pump horsepower. Hp
Q	heat
S	maximum allowable stress
T	temperature, K
T_R	reference temperature
V	volumetric flow rate. GPM

W	work done
X	conversion
Θ	stoichiometric coefficient
η	power efficiency
ρ	density, kg/m^3
ω	compressible flow parameter
CO	carbon monoxide
CO_2	carbon dioxide
et al.	et alias: and others
NaOH	sodium hydroxide

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CHAPTER 1

INTRODUCTION

1.1 History and Application of Benzoic Acid

Benzoic acid was discovered by Nostradamus (1556), and subsequently by Alexius Pedemontanus (1560) and Blaise de Vigenère (1596). However, the structure of benzoic acid only be determined later in year 1832 by Justus von Liebig and Friedrich Wehler. Benzoic acid, can also be known as benzenecarboxylic acid is the simplest aromatic carboxylic acid containing carboxyl group bonded directly to benzene ring, is a white, crystalline organic compound.

It application is widely benefits in our daily lives. Benzoic acid is converted to its salts and esters for the use of preservative application in foods, drugs and personal products. Sodium benzoate, sodium salt of benzoic acid, is used preferably as one of the principal anti-microbial preservatives used in foods and beverages. Sodium Benzoate is also used in medications, anti-fermentation additives and tabletting lubricant for pharmaceuticals. The industrial applications are as a corrosion inhibitor, or as an additive to automotive engine antifreeze coolants and in other waterborne systems, it is used as a nucleating agents for polyolefin. as a dye intermediate, as a stabilizer in photographic processing and as a catalyst. Wide range of benzoic esters are used as solvents, dying carrier, disinfectant additive, penetrating agent and pesticides and manufacturing other compounds. Besides, more than 90% of commercial benzoic acid is converted directly to phenol and caprolactam. Its use in the production of glycol benzoates for the application of plasticizer in adhesive formulations is increasing. It is also used in the manufacture of alkyd resins and drilling mud additive for crude oil recovery applications. It is used as a rubber polymerization activators and retardants. (encyclopedia Benzoic Acid, 2008)

1.2 HYSYS

Aspen Hysys contains data, physical properties, unit operation models, built in default, reports and other features and capabilities developed for specific industrial application. Key Aspen Hysys feature is listed below: (HYSYS documentation, 2002)

1.) Thermo physical properties

    Physical properties model and data are key to generating accurate simulation results. Aspen Hysys used the extensive and proven physical property models, data and estimation methods which cover a wide range of processes.

2.) Convergence analysis

    Automatically analyze and suggest optimal tear streams, flow sheet convergence method and solution sequence for even the largest flow sheets with multiple stream and information recycle.

3.) Sensitivity analysis

    Conveniently generate tables and plots showing how performance varies with changes to selected equipment specifications and operating conditions.

4.) Design specification

Capabilities to calculate operating conditions or equipment parameters to meet specified performance target.

5.) Determine plant operating condition
It will maximize any objective function specified, including process yields, energy usage, stream purities and process economics.

1.3 Problem statement

The production of benzoic acid by oxidation of toluene is used nearly 99% of the worldwide. The latest technology of benzoic acid production is acylation of benzene with acetic anhydride which might be more profitable and could replace the current benzoic acid production process. Besides, in reality the chemical plant are often in unsteady state due to catalytic degradation, equipment fouling and feed disturbances. Optimization is needed to make a better design in order to ensure the process run smoothly without risk.

1.4 The objectives of study

The aim of this study is to design a new process to produce benzoic acid by using benzene and acetic anhydride as raw material. A further objective of this project is to estimate the net profit of this process.

1.5 Scope of study

To achieve objectives, several scopes have been studied.

i.) Base case simulation

By using ASPEN HYSYS 3.2, benzoic acid simulation plant was being developed.

ii.) Optimization

Benzoic acid production was optimized by varying the material flow rate in certain range to monitor the composition of the product.

iii.) Heat integration

This system is used to increase the efficiency of the plant and maximizing the production by varying the process temperature using heat exchanger.

iv.) Physical and chemical properties of chemical substance

To study the chemical reaction and critical properties for each chemical substance which are play important role in the plants.

v.) Cost estimation

To learn how to estimate the production cost and the net profit of the process.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, a general benzoic acid production using benzene, acetic anhydride, sodium hypochlorite and sulphuric acid as an input was reviewed. The idea of this project was to carry out the simulation of benzoic acid production by using ASPEN HYSYS software. Simulation is the process designing a model of a real system and conducting experiments with this model for the purpose either of understanding the behaviour of the system or of evaluating various strategies (within the limits imposed by a criterion or set of criteria) for the operation of the system. The purpose to carry out a simulation for this reaction was to obtain an optimum condition for this reaction. Optimum condition is the certain condition that allows the reaction to achieve a highest yield of product. The main objective of this project was to find out the conditions that can achieve the highest yield product of benzoic acid. The type of conditions were in flow rate, temperature or pressure.

2.2 Green Chemistry

Green chemistry may be defined as the invention, design, and application of chemical products and processes to reduce or eliminate the use and generation of hazardous substances. Practitioners of green chemistry strive to protect the environment by cleaning up toxic waste sites and by inventing new chemical methods that do not pollute and that minimize the consumption of energy and natural resources.

Green synthesis of the future will require making choices about reactants, solvents, and reaction conditions that are designed to reduce resource consumption and waste production. A synthesis is performed in a way that will not consume excessive amounts of resources (and thus use less energy and be more economical) and also will not produce excessive amounts of toxic or harmful by-products, by using a milder reaction conditions.

Ritter (2004) found out that one of the green chemistry approach is to select safer reagents that are used to carry out the synthesis of a given organic compound. For example, sodium hypochlorite (bleach) can be used in some oxidation reactions instead of the highly toxic dichromate/sulphuric acid mixture. (Green Innovations, 2004)

Another approach in green chemistry is to use a reagent that can promote the formation of a given product in less time and with greater yield. Finally, some reagents, especially catalysts, can be recovered at the end of the reaction period and recycled for use again in the same conversion. (Green Innovations, 2004)

Besides, another approach to making organic chemistry greener involves the way in which a reaction is carried out, rather than in the selection of starting material, reagents, or solvents. Microwave technology can be used in some reactions to provide the heat energy required to make the transformation go to completion. With microwave technology, reactions can take place with less toxic reagents and in a shorter time, with fewer side reactions, all goals of green chemistry. (Green Innovations, 2004)

Industrial processes are being designed that are based on the concept of atom economy. Snorri and James (2005) discovered that the Atom economy means that close attention is paid to the design of chemical reactions so that all or most of the atoms that are starting materials in the process are converted into molecules of the desired product rather than into wasted by-products. The atom economy for a reaction can be calculated based on the following equation: (Green Chemistry, 2003)

$$\%atomeconomy = \frac{desired \ldots products(MW)}{All \ldots reac\tan ts(MW)} \times 100\%$$

2.2.1 Replacement of homogenous catalyst with heterogeneous catalyst

Catalysis process research has a tremendous opportunity to reduce the chemical effects to the environment. New catalytic processes that generate less waste, to protect ozone layer, to combat the greenhouse effect, to create environmentally safer transport and to solve environmental problems of energy production will bring development of environmentally safer products.

Generally the acylation reaction was normally catalyzed Lewis acid for example $AlCl_3$, BF_3 and $TiCl_4$ which are homogenous catalyst that widely used in industrial process. However, Lewis acids must be used in higher than stoichiometric amounts and the catalysts must be destroyed at the end of the reaction with a significant production of undesirable wastes. Subrahmanyam and Kumari (2003) state that introduction of zeolites as alternative catalysts has proved to be a major development in the acid catalysed reactions because of their reusability, shape selectivity, high thermal stability and they can be easily tailored to fit the desired reaction. (Catalysis for Energy and Environmentally Benign Technologies, 2003)

According to Castro *et al* (1998), recoverable and re-generable solid acid catalyst such as zeolites Beta can overcome this type of problems. The use of this heterogeneous catalyst is due to the high selectivity of yield, good in separation and the recyclable of the catalyst. Meier *et al.* (1996) found out that due to it acidity, zeolite Beta catalyst can be catalyzed for Friedel-Crafts-acylation reaction. Furthermore, zeolite Beta has a high Si/Al ratio, large pore, high acid strength and thermal stability. As overall conclusion, the heterogeneous catalyst is more efficiency and environmental friendly if compared to homogenous catalyst. (Molecular Catalysis, 1998)

2.2.2 Oxidation of acetophenone by sodium hypochlorite – Green Chemistry

This project is introduced us to new era of green chemistry. Green Chemistry tries to use new reagents or less toxic familiar reagents to be more environmental friendly in place of more hazardous traditional reagents. Currently benzoic acid production is the oxidation of toluene by using potassium permanganate (IV) as an oxidizing agent. This reagent is harmful to environment by releasing the metal ions. A great deal of research is being done and major success stories have been written. One difficulty with green chemistry is finding reagents that perform as well as older reagents.

According to Anderson and Shine (2010), in the past few years in Ramapo College New Jersey, there has been success using Clorox (sodium hypochlorite) reagents but the yield is low if compared to the older reagents. However, the yield can be improved by varying the reaction conditions by simulation. The green advantage of using acetophenone is the products formed are not harmful to the environment and in addition acetophenone is more easily to oxidize by hypochlorite via haloform reaction. (Ramapo College of New Jersey, 2010)

Clorox, a mild oxidant, is a dilute solution of sodium hypochlorite (NaOCl). Clorox should never be mixed with ammonia solutions or ammoniated cleansers as a reaction that releases deadly chlorine gas. (Ramapo College of New Jersey, 2010)

According to Gholam et al (2008) the advantages of using sodium hypochlorite are listed below: (Drake University Department of Chemistry, 2008)

i.) Environmental safe
ii.) Inexpensive oxidants
iii.) Available as grocery store as household bleach
iv.) Easy experimental procedure

2.3 Process description

To prepare benzoic acid, three steps are needed in this project. The first step is acylation of benzene is carried out by the acetic anhydride. Acylation of benzene actually is a heterogeneous catalytic reaction and thus we need to use packed bed reactor (PBR) in order to carry this out reaction. The products of this process are acetophenone and acetic acid. Acetophenone act as an intermediate and will carry forward to another step while acetic acid is a by-product.

Second step is the oxidation of acetophenone by sodium hypochlorite to produce sodium benzoate salt, sodium hydroxide and chloroform which are the by-products. This reaction is carried in a conversion reactor and the sodium benzoate salt is separated out by the hydro cyclone and again will act as an intermediate in order to produce benzoic acid in the next step.

The final step is the acidification of sodium benzoate by sulphuric acid. The products will be main products of this project benzoic acid and sodium sulphate which is the waste disposal of this process. The reaction is carried out in a conversion reactor and benzoic acid will be separated by the hydro cyclone as liquid product from the sodium sulphate salt.

2.3.1 **Friedel-Craft acylation of aromatic compounds** (McMurry, John. 2004)

A Friedel-Crafts acylation is an electrophilic aromatic substitution reaction which introduces an acyl group onto an aromatic ring. The electrophile is an acyl cation that is often coupled to a Lewis acid catalyst, such as aluminium chloride. In order for the reaction to take place, the aromatic ring system must be very electron rich and thus cannot contain any electron withdrawing groups. Below is the diagram of acylation process:

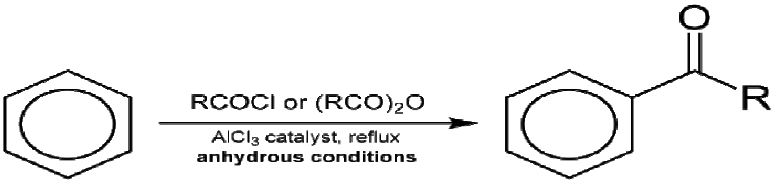


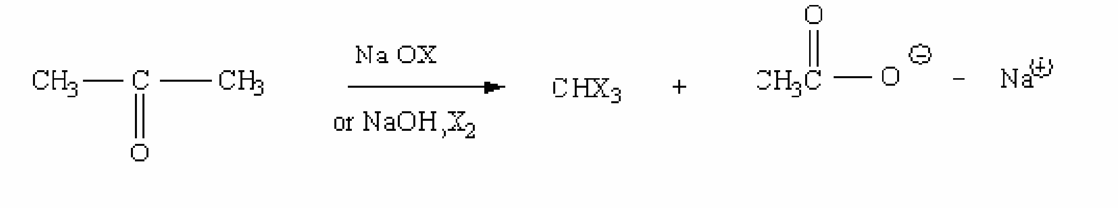
Figure 2.1 Friedel-Crafts acylation

Adams and Noller (2005) discovered that due to the electron-withdrawing effect of the carbonyl group, the ketone product is always less reactive than the original molecule so multiple acylation or other side reaction do not occur.

2.3.2 Oxidation of methyl ketone by haloform reaction (Organic chemistry 2, 1992)

The haloform reaction is so-called because it produced various of halogen product for example chloroform, bromoform and iodoform. Haloform reaction on the methyl ketone actually is an oxidation reaction because it involved he removal of the methyl group which contains hydrogen atom and add in another oxygen atom. The oxidizing agent that we choose in this project is sodium hypochlorite. According to J. W. Zubrick (2005), sodium hypochlorite is effective preparation, ready available and low cost reagent.

Methyl ketones are the only ketones that are useful for preparing carboxylic acids by the haloform reaction. It is essential that a methyl group be attached to the carbon that will become a carboxyl because it is the methyl group that becomes the haloform by-product. The other group attached to the carbonyl becomes the alkyl or aryl portion of the carboxylic acid product. So, the obvious starting material for synthesis of benzoic acid must be acetophenone. Below is the diagram of oxidation of acetophenone by sodium hypochlorite:



The main product is sodium benzoate, by-products are chloroform and sodium hydroxide. Sodium benzoate will be acidified by sulphuric acid in order to get benzoic acid.

2.4 Properties and background of chemicals

2.4.1 Acetic anhydride

Acetic anhydride is a clear, colorless, mobile (free-flowing) liquid with a sharp odor. According to Shakhashiri (2008), an anhydrous ("without water") reagent could lead to better yields of product. This is the reason why acetic anhydride was chosen as material in this project. As with acetic acid, the primary use of acetic anhydride is used in the manufacture of cellulose acetate for films and plastic goods; about 75 percent of the acetic anhydride produced annually in the United States is used for this purpose. Approximately 1.5 percent of the annual acetic anhydride production is used in the synthesis of aspirin. Other uses include the manufacture of industrial chemicals, pharmaceuticals, perfumes, plastics, synthetic fibers, explosives, and weed killers. Because acetic anhydride reacts with water, it is sometimes used as a dehydrating agent in reaction mixtures where removal of water is necessary. (Chemical of the Week, 2008)

2.4.2 Benzene

Benzene is an aromatic hydrocarbon that is produced by the burning of natural products. It is a component of products derived from coal and petroleum and is found in gasoline and other fuels. It is also a principal component of combustion products produced by the burning of PVC (polyvinyl chloride). Benzene is used in the manufacture of plastics, detergents, pesticides, and other chemicals. Benzene also acts as an intermediate in the manufactures of phenol for resins and cyclohexane for nylon. Only smaller amount of benzene are used to make some types of rubbers, lubricants, dyes, detergents, drugs, explosives, napalm and pesticides. (Report of Carcinogens, 2000)

Until World War II, most benzene was produced as a by-product of coke production (or "coke-oven light oil") in the steel industry. However, in the 1950s, increased demand for benzene, especially from the growing plastics industry, necessitated the production of benzene from petroleum. Today, most benzene comes from the petrochemical industry, with only a small fraction being produced from coal. There are four chemical processes contribute to industrial benzene production: catalytic reforming, toluene hydrodealkylation, toluene disproportionation and steam cracking. (Report of Carcinogens. 2000)

2.4.3 Acetic acid

Acetic acid is a clear, colorless liquid with a sharp, irritating odor of vinegar. In poorly heated laboratories, the acid was oftentimes found frozen inside its container because its freezing point is only slightly below room temperature at 16.7C. The term glacial (ice-like) came to be applied to the pure acid in either its solid or liquid state. Glacial acetic acid boils at 118C, and has a density of 1.049 g/mL at 25C. It is flammable with a flash point of 39C. Shakhashiri (2008) discovered that through hydrogen bonding interactions, acetic acid is miscible (mixable) in all proportions with water, ethyl alcohol, and diethyl ether. Pure or concentrated solutions of acetic acid are very corrosive and can cause painful burns. Aqueous solutions of acetic acid freeze at temperatures below the freezing point of water. (Chemical of the Week, 2008)

For many years, the bulk of commercial acetic acid was produced by the oxidation of ethanol. Today, most industrial production of acetic acid is by the Monsanto process, in which carbon monoxide reacts with methanol under the influence of a rhodium complex catalyst at 180C and pressures of 30–40 atm. About 3.2 × 109 kilograms of acetic acid were produced in the United States in 1999. The primary use of this chemical is in the manufacture of assorted acetate esters. These are substances formed by reacting acetic acid with a substance containing a hydroxyl (–OH) group.

Cellulose, found in cotton and wood, is a polymeric material containing multiple hydroxyl groups. It reacts with acetic acid to yield cellulose acetate, which is used to make films and textiles. Some photographic films are made of cellulose acetate, and rayon is made from cellulose acetate fibers. Vinyl acetate, another ester of acetic acid, polymerizes to form poly(vinyl acetate), which is used in water-based latex paints and in glues for paper and wood. (Chemical of the Week, 2008)

2.4.4 Sodium hypochlorite

Sodium hypochlorite is a green/yellow liquid with the characteristic smell of chlorine. It was first used as a bleaching agent and was then discovered to be effective in controlling wound infections. Subsequently, it is most commonly known as household bleach and as a disinfectant, a bleaching agent, in medical treatments and used in the disinfection of drinking water. It is also used for a number of industrial processes such as for commercial laundering, in the manufacture of paper and pulp, for industrial chemical synthesis and disinfection of swimming pools. Perhaps one of the most important applications of sodium hypochlorite is in the disinfection of public water supplies to prevent the transmission of waterborne diseases such as cholera and typhoid. (HPA Compendium of Chemical Hazard, 2008)

Sodium hypochlorite generally is an unstable compound even at normal temperatures, which gradually decomposes naturally. The decomposition rate is accelerated by the elevation of temperature, sunlight especially ultraviolet, heavy metals and the acceleration of pH. Since commercial aqueous solutions are diluted with a large quantity of water, there is no danger of ignition or explosion. Most metals and fibers are corroded by sodium hypochlorite due to its oxidizing properties. Excellent corrosion resistant materials are titanium, glass, and ceramics. Other corrosion resistant materials are rigid polyvinyl chloride, polyvinylidene chloride, polyethylene, fluororesin, flexible polyvinyl chloride, and ebonite. Rubbers are less resistant to corrosion by sodium hypochlorite. (Japan Soda Industry Association, 2008)

2.4.5 Sulphuric acid

Commercial sulphuric acid is sometimes colourless but, it is often yellow and its colour ranges from pale to dark brown shades. In dilute solution, it is highly corrosive and attacks nearly all metals. Dilute solution of sulphuric acid show all the behaviour characteristics of acids. They taste sour, conduct electricity, neutralize alkalines and corrode active metals with the formation of hydrogen gas. It used as drying agent, acidifying agent (pH control), hydrolyzing agent, neutralizing agent, dehydrating agent, oxidizing agent, absorbing agent, purifying agent, leaching agent, catalyst and active reagent is petrochemical industries.

There are two major processes which are lead chamber and contact process for production of sulphuric acid, are available commercially in a number of grades and concentration. The lead chamber process, the older of the two processes, is used to produce much of the acid used to make fertilizers; it produces a relatively dilute acid (62%-78% H_2SO_4). The contact process produces a purer, more concentrated acid but requires purer raw materials and the use of expensive catalysts. (Encyclopedia, 2008)

Sulphuric acid is one of the most important industrial chemicals. More of it is made each year than is made of any other manufactured chemical; more than 40 million tons of it was produced in the United States in 1990. The major use of sulfuric acid is in the production of fertilizers, for example superphosphate of lime and ammonium sulfate. It is widely used in the manufacture of chemicals in making hydrochloric acid, nitric acid, sulfate salts, synthetic detergents, dyes and pigments, explosives, and drugs. Besides, it is also used in petroleum refining to wash impurities out of gasoline and other refinery products. (Encyclopedia, 2008)

2.4.6 Chloroform

Chloroform is a colourless, volatile liquid that is non-flammable. It is slightly soluble in water and is miscible with oils, ethanol, ether, and other organic solvents. Chloroform has a pleasant, non-irritating odour. It is unstable when exposed to air, light, and/or heat, which cause it to break down to phosgene, hydrochloric acid, and chlorine. It is usually stabilized by the addition of 0.5% to 1% ethanol. When heated to decomposition, chloroform emits toxic fumes of hydrochloric acid and other chlorinated compounds (WHO 1994, HSDB 2001).

In industry, chloroform normally is produced by the chlorination of methyl chloride at high temperatures or through the haloform reaction which the sodium hypochlorite as a reagent. McCulloh (2003) discovered that chloroform is manufactured mainly in United State and the total capacity in the late 1990s being about 520000 tons per year. An estimated 95% of the global consumption of chloroform is in the manufacture of hydrochlorofluorocarbons, specifically HCFC-22, which is widely used in refrigeration and air conditioning applications because of its excellent physical and thermodynamic properties. HCFC-22 is also used in the production of fluoropolymers and as a blowing agent for rigid expanded polystyrene (XPS) foam insulation. The remaining 5% of chloroform produced globally is used in the synthesis of pharmaceuticals and agricultural products, and as laboratory reagents.

2.4.7 Chlorine

Chlorine is a toxic, corrosive, greenish yellow gas with a pungent, irritating odour. Chlorine is produced mostly by electrolysis of brine; some is obtained as a by-product in the manufacture of sodium metal by the electrolysis of sodium chloride either molten or in solution. It was, in fact, one of the first poisonous gases used in warfare—in 1915 during World War I. In spite of its disagreeable nature, there are so many everyday products that contain chlorine or are manufactured through the use of chlorine that it is among the top ten chemicals produced in the United States each year. In 1994, more than 24 billion lb (11 billion kg) of chlorine were produced. (United State Protection Agency, 1999)

Chlorine is an important chemical in water purification, in disinfectants, in bleach and in mustard gas. Chlorine is also used widely in the manufacture of many products and items directly or indirectly, for example in paper product production, antiseptic, dyestuffs, food, insecticides, paints, petroleum products, plastics, medicines, textiles, solvents, and many other consumer products. It is used to kill bacteria and other microbes from drinking water supplies. Chlorine is involved in beaching wood pulp for paper making, bleach is also used industrially to remove ink from recycle paper. (United State Protection Agency, 1999)

2.4.8 Sodium hydroxide

Sodium hydroxide is industrially produced as a 50 % solution by variations of the electrolytic chloro-alkali process. Chlorine gas is also produced in this process. Solid sodium hydroxide is obtained from this solution by the evaporation of water. Solid sodium hydroxide is most commonly sold as flakes, prills, and cast blocks. In 2004, world production was estimated at 60 million dry metric tonnes of sodium hydroxide, and demand was estimated at 51 million tonnes. Sodium hydroxide may be formed by the metathesis reaction between calcium hydroxide (also known as lime) and sodium carbonate (also known as soda ash). The major use of sodium hydroxide is in the manufacture of other chemicals. It is widely use in textile industry, production of viscose rayon, production of soap and detergents, and used for sodium hypochlorite which is used as a household bleach. (Encyclopedia, 2008)

Shalok and Kaley (2003) discovered that sodium hydroxide itself is non-combustible material but if sodium hydroxide mixed with water, it may generate enough heat to ignite the combustible materials. Sodium hydroxide reacts with all mineral and organic acids, forming the corresponding salts. The heat generated may be sufficient to raise the temperature above the boiling point, resulting in sporadic, dangerous of the solution. Besides, sodium hydroxide also reacts with metals such as aluminium and zinc to generate flammable hydrogen gas. (Technical Supporting Documents, 2003)

2.5 Material Safety Data Sheet (MSDS) of chemicals

Table 2.1 Environmental and health effects of chemicals

Chemicals	Environmental effects	Health effects
Acetic anhydride (OSHA, 2008)	- Toxic gases and vapours (such as CO_2, CO, various hydrocarbons and acid aerosol) may be released if decomposed. - When released into water, this material is expected to react with water to form acetic acid which decreased the pH of the water.	- Proctor et al (1988) found that if exposed to higher than 5ppm experienced acute eye and upper respiratory tract irritation. - Grayson (1985)discovered that causes delayed burn when contact with skin
Benzene (OSHA, 2008), (National Pollutant Inventory, 1992)	- It will breakdown and mobile quickly when released into soil. - Slightly soluble in water but is absorbed by lipid phase of aquatic organism which results in transport in the environment	- Long term exposure can result in various blood disorder, ranging from anemia to leukemia, an irreversible and fatal disease.
Acetic acid (OSHA, 2008), (National Pollutant Inventory, 1992)	- High concentration means highly corrosive which can be harmful to animals, plants and aquatic life.	- Liquid or spray may produce damage particularly on mucous membrane of eyes, mouth and respiratory tract.
Sodium hypochlorite (JapanSoda Industry Association, 2008), (OSHA, 2008), (National Pollutant Inventory, 1992)	- Chlorine gas and chloroamines will be produced when mixed with acidic products or ammonia cleansers. Chlorine and chloromines are toxic to aquatic organism. - From overall it is an environment	- Hypochlorous acid is isolated and irritates the human skin and mucous membranes, but there is hardly systemic poisoning due to absorption.

	friendly chemical.	
Sulphuric acid (National Pollutant Inventory, 1992)	- It will bring acid rains by dissolve in cloud, fog or rain. - Acid rains bring toxicity to aquatic organisms and plants.	- Exposure to mist can irritate the eyes, nose, throat and lungs, and at higher levels can cause pulmonary oedema.
Chloroform (Environment Agency, 2011), (OSHA, 2008)	- It involved in reactions with other air pollutants that form ground level ozone, which can cause damage to crop and material - From overall it is not likely o cause significant impact	- Inhalation of chloroform causes central nervous depression - Clayton (1982) found put that exposure of pregnant women to chloroform may results in malformation
Chlorine (OSHA, 2008), (Lentech water treatment and purification, 2009)	- Once in air or water, it hydrolyses to hypochlorous acids which are harmful to organisms living in water and soil. - No significance effect to animals and plants since they are not likely to store chlorine.	- Genium (1992) state that high level of chlorine can decrease the organ and body weight in animal. The main concern is the increased likelihood of cancer induction.
Sodium hydroxide (OSHA, 2008), (Technical Support Document: Sodium Hydroxide, 2009)	- If release to air it will combines with water vapour, and the resulting aerosol or mist will be corrosive. - Contamination of groundwater is not likely to happen since it is highly reactive and is rapidly neutralized by organic materials in soil.	- High concentrations are irritating to the upper respiratory tract and may result in pulmonary edema. - Skin contact with sodium hydroxide granules cause chemical and thermal burns leading to deep tissue injury.

2.6 Summary

Generally there are many articles and journals have been published on benzoic acid production. In this research, the production of benzoic acid was decided by using benzene, acetic anhydride and sodium hypochlorite. The reason was because acylation of benzene by acetic anhydride can result higher yield due to the anhydrous properties of acetic anhydride. In addition, the low cost and environmental friendly of sodium hypochlorite is also the main factor for production of benzoic acid.

CHAPTER 3

MENTHODOLOGY

3.1 Research Tools

This research was carried out using various computational tools. Aspen HYSYS 3.2 simulator was used for process flow sheeting to provide data regional analyses. Aspen HYSYS 3.2 simulator was also used to perform the new process model for benzoic acid production using acetic anhydride and benzene as a raw material for fuel cell application.

3.1.1 Aspen Hysys

Aspen Hysys is a component of the Aspen Engineering Suite (AES). The process simulation capabilities of Aspen Hysys enables engineers to predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. With reliable thermodynamic data, realistic operating conditions and the rigorous Aspen Hysys equipment models, they can simulate actual plant behavior.

3.1.2 Modeling and Simulation of benzoic acid production

The benzoic acid production from benzene and acetic anhydride was simulated using Hysys software. Typically, the simulation processes took the following stages:

1.) Preparation stage
    a.) Define chemical component
    b.) Select a thermodynamics package
    c.) Add and define the reaction

2.) Building stage
    a.) Add and define streams
    b.) Add and define unit operations
        i.) Packed bed reactor
        ii.) Distillation column
        iii.) Oxidation reactor
        iv.) Acidification reactor
        v.) Hydro cyclone
    c.) Connecting streams to unit operations
    d.) Add auxiliary units
        i.) Heat exchanger
        ii.) Cooler

3.) Execution
    a.) Starting simulation
    b.) Optimization for each part

Based on bench-scale testing, the following process parameters are expected.

Feedstock Consumption
Acetic anhydride: 50 kgmole/h
Benzene: 50 kgmole/hr

Process Conditions
Temperature: 50 ℃
Pressure: 101 kPa

3.2 Mathematical Modelling of the reactor operating

A linear first-order Ordinary Differential Equation (ODE) can be described as follows:

$$\tau \frac{\partial Y}{\partial t} + Y = Kf(y) \qquad (3.1)$$

In a non-linear equation, the process variable *Y* may appear as a power, exponential, or is not independent of other process variables. Here are two examples:

$$\tau \frac{\partial Y}{\partial t} + Y^3 = Kf(y) \qquad (3.2)$$

$$\tau \frac{\partial Y}{\partial t} + YY_2 = Kf(y) \qquad (3.3)$$

The great majority of chemical engineering processes occurring in nature are nonlinear. Nonlinearity may arise from equations describing equilibrium behaviour, fluid flow behaviour, or reaction rates of chemical systems. While a linear system of equations may be solved analytically using matrix algebra, the solution to a non-linear set of equations usually requires the aid of a computer.

3.2.1 **Reactor Sizing (**Fogler, 2004)

The reactor involved in this plant is continuous flow reactor or tubular reactor. In tubular reactor, Fogler (2004) discovered that the reactants are continually consumed as they flow down the length of the reactor. Thus, the conversion of reactant will increase along the length of the reactor. In this case the reaction is

$$A + B \rightarrow C + D$$

The mole balance equation for species A in the reaction was expressed as

$$-\frac{\partial F_A}{\partial V} = -r_A$$

For a flow system, F $_A$ has previously been given in terms of the entering molar flow rate F_{AO} and the conversion X

$$F_A = F_{AO} - F_{AO}X \qquad (3.4)$$

Differentiate it into

$$\partial F_A = -F_{AO}\partial X \qquad (3.5)$$

Substitute equation above into equation 1 to give

$$F_{AO}\frac{\partial X}{\partial V} = -r_A \qquad (3.6)$$

The variables was separated and integrated with the limits V=0 when X=0 to obtain the PBR volume necessary to achieve a specified conversion X

$$V = F_{AO}\int_0^X \frac{\partial X}{-r_A} \qquad (3.7)$$

In this case the conversion is 99%, thus

$$V = F_{AO}\int_0^{0.99} \frac{\partial X}{-r_A} \qquad (3.8)$$

By using Simpson-three-eight rules,

$$V = \frac{3\Delta X}{8}F_{AO}\left[\frac{1}{-r_A(X=O)} + \frac{3}{-r_A(X=0.33)} + \frac{3}{-r_A(X=0.66)} + \frac{1}{-r_A(X=0.99)}\right] (3.9)$$

From the simulation results we obtained,

X	0.00	0.33	0.66	0.99
1/-r $_A$ ($m^3.hr/kgmole$)	269.1	79.2	48.9	10650.8

Table 3.1 Process data for PBR reactor

Substitute the value into the numerical equation,

$$V = \frac{3(0.99)}{8}\left(100\,{}^{kgmole}\!\!\diagup_{hr}\right)\left[269.1 + 3(79.2) + 3(48.9) + 10650.8\right]\left\{m^3.s\diagup_{kgmole}\right\}\left\{\frac{1hr}{3600s}\right\}$$

$$= 117.8\ \mathrm{m}^3 \approx 120m^3$$

As a result, the reactor volume necessary to achieve 99% conversion was $120m^3$.

3.2.2 **Energy balances** (Fogler, 2004)

Fogler (2008) discovered that the energy balance for continuous flow reactor can be described by the first law of thermodynamics. For an open system in which some of the energy exchange is brought about by the flow of mass across the system boundaries, the energy balance can be expressed as:

Rate of accumulation of total energy = Flow of total energy into system - Flow of total energy out of system + Heat added to system across its boundary + Heat generated by reaction - Work done by system on surroundings

The flow of energy into or out of the system is by convection or conduction. Heat added to the system across its boundaries by conduction or radiation. For a steady-state tubular flow reactor the energy balance can be expressed as

$$Q - W_S - F_{AO}\sum_{i=1}^{n}\Theta_i C_{Pi}(T - T_{i0}) - \left[\Delta H_{Rx}^{o}(T_R) + \Delta C_P (T - T_R)\right]F_{AO}X = 0 \qquad (3.10)$$

Where

Q = Rate of heat flow

W = Work done by the system

F_{AO} = Reactant initial molar flow rate

T = Operating temperature or outlet temperature

T_R = Reference temperature

X = Conversion

C_P = Heat capacity

ΔH_{Rx}^{o} = Heat of reaction

Θ = Stoichiometric coefficient

Consider plug flow reactor as an example, the reaction is

$$C_6H_6 + C_4H_6O_3 \rightarrow C_6H_5COCH_3 + CH_3COOH$$

Table 3.2 Heat capacities and heat of formation data for various chemical reactants

Substance	Heat of formation (kJ/kg mole)	Heat capacities (kJ/kg mole.C)
Benzene	82980	126.1
Acetic anhydride	-576100	188.6
Acetophenone	-86920	253.3
Acetic acid	-435100	103.3

Heat of reaction $(\Delta H_{Rx}^{o}(T_R))$ = Heat of formation (product) – Heat of formation (reactant)

= (-435100) + (-86920) – [(-576100) + 82980]

= **-28900 kJ/kg mole**

$\Delta C_P = C_{Pi} - C_{Pi0}$ = 253.3 + 103.3 – 126.1 – 188.6 = **42 kJ/kg mole. C**

$$\sum_{i=1}^{n} \Theta_i C_{Pi} = (1)(126.1) + (1)(188.6) = 314.7$$

In this case, the reactor is adiabatic. So Q = W = 0. The energy balance equation will be reduced to

$$-F_{AO}\sum_{i=1}^{n} \Theta_i C_{Pi}(T - T_{i0}) - \left[\Delta H^o_{Rx}(T_R) + \Delta C_P(T - T_R)\right]F_{AO}X = 0 \qquad (3.11)$$

With F $_{AO}$ = 100 kg mole/hr and X = 0.99,

$$\left(-100\,{}^{kgmole}\!/_{hr}\right)\left(314.7\,{}^{kJ}\!/_{kgmole.C}\right)\left(105.6^o C - 25^o C\right)$$

$$-\left[\left(-28900\,{}^{kJ}\!/_{kgmole}\right) + \left(42\,{}^{kJ}\!/_{kgmole.C}\right)\left(105^o C - 25^o C\right)\right]\left(100\,{}^{kgmole}\!/_{hr}\right)(0.99)$$

$-2536482 + 2525965 \approx 0$

3.2.3 **Degree of freedom** (Felder et al, 2000)

There are two types of degree of freedom. The first one is dynamic degrees of freedom, N_m (m denotes manipulated). Second is steady state degrees of freedom, N_{ss} . To obtain the number of steady state degrees of freedom, the subtract from N_{om} which was the number of manipulated variables with no steady state effect and N_{oy} which was the number of variables that need to be controlled from N_m

$$N_{SS} = N_M - \left(N_{OM} + N_{OY}\right) \qquad (3.12)$$

In any process simulation work, it is essential that the degrees of freedom analysis be carried out to determine the number of variables to be specified.

3.2.4 **Material balance** (Felder et al, 2000)

The conservations relationships are the basis of mathematically modeling in HYSYS. It is the accumulation term which allows the output variables from the system to vary with time. Felder and Rousseau (2000) discovered that the conservation of mass is maintained in the following general relation:

Rate of accumulation of mass = mass flow into system - mass flow out of system + rate of generation by chemical within the system

$$F_i - F_O + r\Delta V = \frac{\partial N_j}{\partial t} \qquad (3.13)$$

Where

F_i = feed mass flow rate

F_O = Product mass flow rate

$r\Delta V$ = mass rate of generation

$\frac{\partial N_j}{\partial t}$ = mass rate of accumulation

Consider the oxidation reactor as an example, the mass rate of generation and mass rate of accumulation is neglected in steady state. Thus the equation is reduced to

$$F_i = F_O$$

Table 3.3 Mass flow rate for various material and product streams in HYSYS

Substance	Mass flow rate (kg/hr)
Acetophenone	12010
Sodium hypochlorite	33540
Vap	21090
Liq	24460

From the results obtained,

$$12010 + 33540 = 21090 + 24460$$

$$45550 = 45550$$

3.2.5 **Efficiency of hydro cyclone separation** (Martin Rhodes, 2008)

Martin Rhodes (2008) did a survey on the efficiency separation if he hydro cyclone. The efficiency could be related to the following equation:

$$E_T = \frac{M_C\left(\partial F_C/\partial x\right)}{M\left(\partial F/\partial x\right)} \tag{3.14}$$

Where

E_T = Separation efficiency

M = feed mass flow rate

M_C = coarse product mass flow rate

$\left(\partial F_C/\partial x\right)$ = mass fraction of solid in coarse product

$\left(\partial F/\partial x\right)$ = mass fraction of solids in feed

Consider hydro cyclone 2 as an example

Table 3.4 Mass flow rate and fraction for Hydro cyclone-2 in HYSYS

Stream name	Mass flow rate (kg/hr)	Mass fraction
Liq prods (feed)	20620	0.267
Sodium sulphate (coarse product)	8451	0.656

$$E_T = \frac{\left(8451\,{}^{kg}/_{hr}\right)(0.656)}{\left(20620\,{}^{kg}/_{hr}\right)(0.267)} = 0.99$$

The efficiency obtained was satisfied with the simulation result.

3.3 **Thermodynamics properties** (Robin Smith, 2007)

In order to define the process, the thermodynamics property packages used to model steady-state of benzoic acid production must be specified. The suitable thermodynamics package in this benzoic acid production is UNIQUAC method. Robin and Smith (2007) found that the reason for UNIQUAC method was being selected because this method is to model liquid phase non-ideality reaction at moderate pressure. The UNIQUAC equation is given by:

$$\ln \gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + l_i - \frac{\Phi_i}{x_i} \sum_j^{NC} x_j l_j + q_i \left[1 - \ln\left(\sum_j^{NC} \theta_j \tau_{ji}\right) - \sum_j^{NC} \frac{\theta_j \tau_{ij}}{\sum_k^{NC} \theta_k \tau_{kj}}\right]$$

Where

u_{ij} = interaction parameter between molecule i and molecule j

z = coordination number (z=10)

r_i = pure component property, measuring the molecular van der Waals volume for Molecule i

q_i = pure component property, measuring the molecular van der Waals surface area for Molecule i

R = gas constant

T = absolute temperature

$$\Phi_i = \frac{r_i x_i}{\sum_k^{NC} r_k x_k} \qquad \theta_i = \frac{q_i x_i}{\sum_k^{NC} q_k x_k}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1)$$

$$\tau_{ij} = \exp - \left(\frac{u_{ij} - u_{jj}}{RT}\right)$$

For steady-state modeling of benzoic acid production, the UNIQUAC Equation of state was found to simulate benzoic acid production faster than the real time.

3.4 Summary

As summary, this chapter was mainly about the development of the simulation using ASPEN HYSYS 3.2. The thermodynamics package need to be chosen before begins the simulation and all energy and mass balances have established for all cases. Below is the block diagram for the simulation sequences.

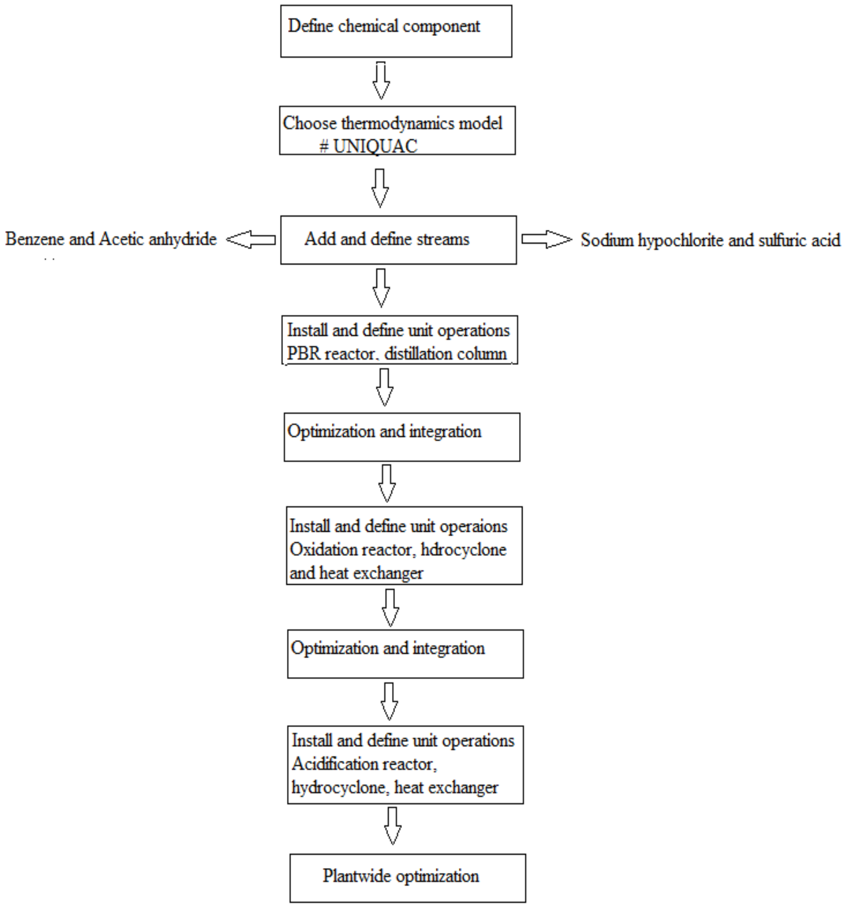


Figure 3.1 Block diagram of the benzoic acid plant simulation using ASPEN HYSYS

CHAPTER 4

RESULTS AND DISCUSIONS

4.1 Optimization for base case study

The base case of this study was developed by the introduction of the raw materials into the packed bed reactor (PBR). The raw materials used were acetic anhydride and benzene. The variables to be optimized were the acetic anhydride flow rate and packed bed reactor feed temperature in order to monitor the composition and molar flow of the products. The process was carried in liquid form and the reactor and distillation column was set to 101kPa which is atmospheric pressure.

4.1.2 Results of base case feed temperature optimization

Initially both of the materials were in liquid phase at room temperature $25^\circ C$. The reactor pressure was set to 101kPa because in this reaction the pressures do not have significant effect since the reaction is under liquid phase. On the other hands, from table 4.1, by varying the feed temperature from the range $0^\circ C$ to $100^\circ C$, the composition and molar flow of the distillate and bottom liquids were observed to be the same. In this case, the temperature did not play an important role in this reaction. Thus this reaction could undergo under room temperature. This could save the equipment cost utility costs because the process was run in the condition without the heat exchanger. Below are the results for different temperature:

Table 4.1 Results of distillate and bottom liquids molar flow and component mole fraction for different temperature

Temperature (°C)	Distillate molar flow rate (kg mole/hr)	Distillate acetic acid component mole fraction	Bottom liquids molar flow rate (kg mole/hr)	Bottom liquids acetophenone component mole fraction
20	50.14	0.9967	49.86	0.9999
40	50.15	0.9966	49.85	0.9999
60	50.17	0.9962	49.83	0.9999
80	50.27	0.9941	49.72	0.9999
100	59.64	0.8380	40.36	0.9999

4.1.2 Results of optimization by variation of material molar flow rate

The optimized materials were acetic anhydride in order to obtain the highest purity and yield for acetic acid and acetophenone. The basis for benzene was set to 50 kg mole/hr. The variation range for acetic acid molar flow rate was between 10 kg mole/hr to 100 kg mole/hr at room temperature. From table 4.2, the most suitable flow rate for acetic anhydride was 50 kg mole/hr. For this acetic anhydride flow rate, the highest composition and molar flow rate for both the acetic acid and acetophenone could be obtained. The purity for acetic acid was 99.67% while purity for acetophenone is 99.99%. Besides, both of the molar flow rates of acetic acid and acetophenone were 50 kg mole/hr (50% yields). The results for different acetic anhydride flow rate were showed in table 4.2:

Table 4.2 Distillate and bottoms liquids molar flow and component mole fraction for different acetic anhydride molar flow rate

Acetic anhydride molar flow rate (kg mole/hr)	Distillate molar flow rate (kg mole/hr)	Distillate acetic acid component mole fraction	Bottom liquids molar flow rate (kg mole/hr)	Bottom liquids component mole fraction
10	50	0.2	10	0.9999
30	50	0.6	30	0.9999
50	50	0.9967	50	0.9999
70	71.3	0.7005	48.67	0.9999
90	92	0.5437	48.12	0.9999

4.1.3. Distillation column specification

In order to get the high purity, the separation by using distillation column was needed. From the stimulation, the number of stages required for this distillation column was determined to be ten (10) and the feed stage location was plate number five (5) from the top. This number of stages and feed stage location was chosen because it can satisfy all the specifications made throughout the whole stimulation. A pump was need to add before enter the distillation column. Seader and Henley (2006) did a survey on the feed pressure must be greater than the column pressure to prevent the feed partially vaporize before enter the distillation column. Two specifications were use in this distillation column, percentage of acetophenone recovery and reflux ratio. In this case, the 99% acetophenone recovery was specified in acetophenone stream and one for the reflux ratio.

The reflux ratio defined as the ratio of the amount of moles returned as refluxed liquid to the fractionating column and the amount of moles of final product, both per unit time. By adjusting the reflux ratio, the composition of the acetic acid in distillate could be improved. Theoretically, the more reflux provided for a given number of theoretical stages, the better the column separation. Then, the reflux ratio was increased to 10. The recovery of the components was much better compared to the previous one. The diagrams below have showed the comparison of composition when different reflux ratio. The composition of acetic acid was 0.9273 for reflux ratio 0.1 and 0.9999 for reflux ratio 10. This shows the differences of acetic acid composition by varying the reflux ratio. However, Seader and Henley (2006) discovered that the reboiler steam and condenser cooling water requirements increased with the increasing of reflux ratio. This had caused the power of both condenser and reboiler increase and resulted in high utilities cost. There were not much different for acetic acid and acetophenone composition between reflux ratios 1 and 10. Thus the reflux ratio one was chosen in order to reduce the utilities cost. The results for different reflux ratio showed in table 4.3.

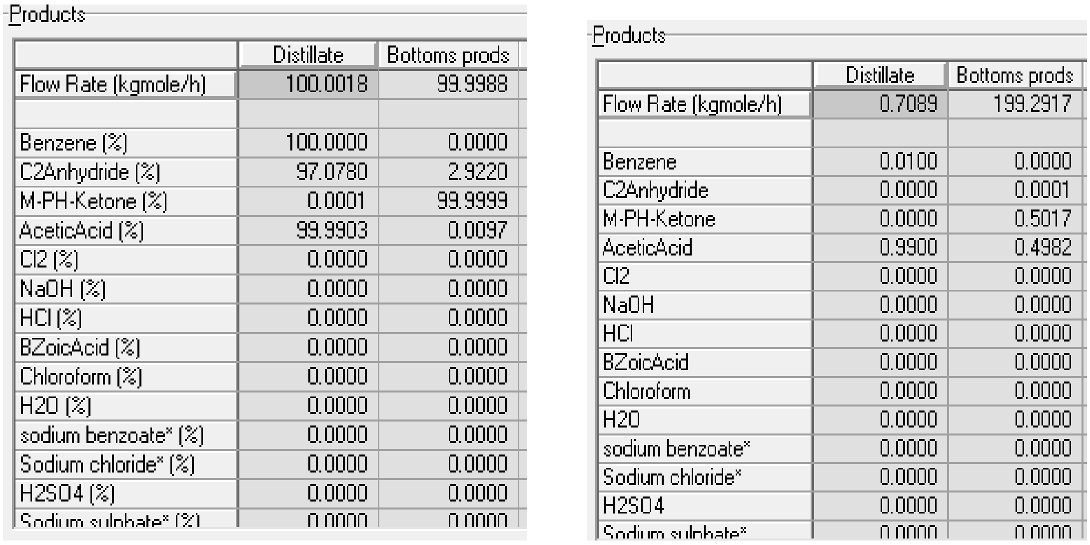
Table 4.3 Relationship between reflux ratio, composition and power

Reflux ratio	Acetophenone component mole fraction	Acetic acid component mole fraction	Total power of reboiler and condenser (kW)
0.1	0.9999	0.9273	1912
1	0.9999	0.9967	2357
10	0.9999	0.9993	7628

Other than reflux ratio specification, the component mole fraction specification was also found in the distillation column. There were two options here, one was specify the distillate acetic acid composition as 0.99 or specify the bottom products acetophenone composition as 0.99. There was some significance between the two specifications. If specified the acetic acid composition in distillate is 0.99, the components were all recovered in bottom liquids. It did not fit the purpose of building the distillation column to separate the components. On the other hands, if specified the acetophenone composition in bottom liquids as 0.999, the percentage recoveries of all components were also found at least 99%. Besides it could separate the acetic acid and acetophenone with each of them 50% yield. This could fulfill the purpose to build the distillation column and the aim to obtain 99.99% purity of acetophenone and acetic acid.

Thus, specification acetophenone composition in bottoms liquid was the suitable choice. Below is the diagrams show the percentage recovery by using different specifications.

Figure 4.1 (a) and (b)



Products

	Distillate	Bottoms prods
Flow Rate (kgmole/h)	100.0018	99.9988
Benzene (%)	100.0000	0.0000
C2Anhydride (%)	97.0780	2.9220
M-PH-Ketone (%)	0.0001	99.9999
AceticAcid (%)	99.9903	0.0097
Cl2 (%)	0.0000	0.0000
NaOH (%)	0.0000	0.0000
HCl (%)	0.0000	0.0000
BZoicAcid (%)	0.0000	0.0000
Chloroform (%)	0.0000	0.0000
H2O (%)	0.0000	0.0000
sodium benzoate* (%)	0.0000	0.0000
Sodium chloride* (%)	0.0000	0.0000
H2SO4 (%)	0.0000	0.0000
Sodium sulphate* (%)	0.0000	0.0000

Products

	Distillate	Bottoms prods
Flow Rate (kgmole/h)	0.7089	199.2917
Benzene	0.0100	0.0000
C2Anhydride	0.0000	0.0001
M-PH-Ketone	0.0000	0.5017
AceticAcid	0.9900	0.4982
Cl2	0.0000	0.0000
NaOH	0.0000	0.0000
HCl	0.0000	0.0000
BZoicAcid	0.0000	0.0000
Chloroform	0.0000	0.0000
H2O	0.0000	0.0000
sodium benzoate*	0.0000	0.0000
Sodium chloride*	0.0000	0.0000
H2SO4	0.0000	0.0000
Sodium sulphate*	0.0000	0.0000

(a) Acetophenone composition specification of 99% mole fraction

(b) Acetic acid composition specification 99% mole fraction

4.2 Optimization of conversion reactor

This was the second part of the process. The process was started when the acetophenone form the first part and sodium hypochlorite is fed into the conversion reactor. The reaction was produced sodium benzoate together with the sodium hydroxide in bottom products while chloroform was produced as overhead products. The bottom products were fed into hydro cyclone to separate the sodium benzoate from sodium hydroxide and chloroform was fed to the separator in order to separate it from water. The main purpose in this section was to optimize the yield and the purity of sodium benzoate produced by the by hydro cyclone.

4.2.1 Results of optimization for variation of sodium hypochlorite molar flow rate

Initially the quantity of acetophenone produced from the first part of the process contains 50 kg mole/hr. Thus, in order to achieve the maximum purity and yield for both chloroform and sodium benzoate, the molar flow rate of sodium hypochlorite need to be optimized. The range of sodium hypochlorite molar flow rate was set within 150 to 1500 kg mole/hr. From the figure 4.9, the conversion rate is proportional to the sodium hypochlorite molar flow rate and then it achieved maximum conversion at 1200 kg mole/hr. So the best molar flow rate was 1200 kg mole/hr. At this flow rate, the reactor was operating at maximum conversion. Thus, maximum purity and yield of products could be achieved. In a study of chemical reaction engineering (Fogler, 2008) the reason for high molar flow rate of sodium hypochlorite need to use was because the stoichiometric coefficient was directly proportional to the molar flow rate. When the stoichiometric coefficients increased, the molar flow rate need to be used will increase also. According to the chemical equation, the stoichiometric coefficient for sodium hypochlorite was three if compared to acetophenone stoichiometric coefficient which was one. This indicates that the quantity of sodium hypochlorite we need to use is more than the acetophenone in order to achieve optimum conversion. For instance,

$$A + 3B \rightarrow C + D$$

The initial molar flow rate was calculated by the following equations:

$F_{BO} = F_{AO}\Theta_B = 3F_{AO}$ $\quad F_{CO} = F_{AO}\Theta_C$ $\quad F_{DO} = F_{AO}\Theta_D$

where Θ = stoichiometric coefficient F= molar flow

From the above equations if the initial flow rate of A was 50 kg mole/hr, the initial flow rate for B was 150 kg mole/hr. Below are the results of conversion rate and sodium benzoate component mole fraction for different sodium hypochlorite molar flow rate.

Table 4.4 Conversion rate and composition of chemical substance inside the oxidation reactor

Sodium hypochlorite molar flow rate (kg mole/hr)	Conversion (%)	Sodium benzoate component mole fraction	Acetophenone component mole fraction
300	24.83	0.2187	0.0192
600	49.65	0.2196	0.0100
900	74.48	0.2203	0.0040
1200	99.00	0.2205	0.0001
1500	99.00	0.2049	0.0001

From the table above, the acetophenone component mole fraction decreased while sodium benzoate component mole fraction increased with the increasing of sodium hypochlorite molar flow rate. The acetophenone was fully utilized at 1200 kg mole/hr, thus if the sodium hypochlorite molar flow rate was exceeded 1200 kg mole/hr, it would dilute the mixture and eventually lower the sodium benzoate mole fraction.

4.2.2 Results of heat integration for conversion reactor

Initially the temperature of acetophenone was $377.6^{\circ}C$ while the temperature for sodium hypochlorite was at room temperature. The mixture from this component is at $60^{\circ}C$. Now the conversion reactor feed temperature was settled within the range $50^{\circ}C$ to 1000 $^{\circ}C$. After optimization, the optimum temperature is found to obtain maximum yield and purity of sodium benzoate was at temperature $700^{\circ}C$. Kurt and George (2007) found that the reaction rate that involves sodium hypochlorite was increased by elevation of the temperature. This was because the reaction rate increased with the reduced of hypochlorite concentration and increased of pH. In this case the concentration of hypochlorite is 12.5% for industrial uses and there is also some chlorine was also present in the solution. This would reduce the pH at the same time. Thus the temperature must be increased in order to vaporize the chlorine and as a result the pH would be increased. Below are the results of sodium benzoate, acetophenone and chlorine component mole fraction at different temperature.

Table 4.5 Composition of various chemical substances in oxidation reactor at different temperature

Temperature (C)	Sodium benzoate component mole fraction	Acetophenone component mole fraction	Chlorine component mole fraction
100	0.0318	0.0003	0.0767
300	0.0980	0.0006	0.0096
500	0.1924	0.0004	0.0029
700	0.2049	0.0001	0.0011
900	0.2071	0.0001	0.0006

4.2.3 Comparison of optimization results

Below are the results of optimization after the reaction was completed and separated by the hydro cyclone.

Table 4.6 Results after and before optimization

	Before Optimization	After Optimization
Sodium benzoate component mole fraction	0.2391	0.5219
Sodium hydroxide component mole fraction	0.2715	0.9717
Sodium benzoate molar flow rate (kg mole/hr)	10.71	93.61
Sodium hydroxide molar flow rate (kg mole/hr)	61.86	147.2
Sodium hypochlorite molar flow rate (kg mole/hr)	150	1200
Temperature (°C)	58	700

Tables 4.6 had compared results of the effluent produced before and after the optimization. The increase in sodium hypochlorite molar flow rate and conversion reactor feed temperature give the higher purity and yield for each component. Sodium hydroxide was the by-products while sodium benzoate was the intermediate and would be carried forward into next process to produce benzoic acid.

4.3 Optimization of acidification reactor

Acidification of sodium benzoate is the final part of the process. This process involved a conversion reactor and hydro cyclone. After the reaction take place in the reactor the outcome will be fed into the hydro cyclone in order to separate benzoic acid from the salts. In this section, the main purpose was to optimize the yield and purity of final product benzoic acid by varying the sulphuric acid molar flow rate and the conversion reactor feed temperature.

4.3.1 Results of optimization by varying the sulphuric acid molar flow rate

The molar flow of sodium benzoate was settled as basis 93.61 kg mole/hr. At the same time, the range of sulphuric acid molar flow rate was settled within 10 kg mole/hr to 100 kg mole/hr. After optimization, the sulphuric acid molar flow rate was chosen at 30 kg mole/hr. At this flow rate, the benzoic acid component mole fraction was 0.3952 and the molar flow rate was 123.6 kg mole/hr. The conversion rate is 81.43%. For more details can refer to section 4.2.1. Below were the results of benzoic acid component mole fraction and conversion rate at different sulphuric acid molar flow rate.

Table 4.7 Benzoic acid component mole fraction and conversion rate at different temperature

Sulphuric acid molar flow rate (kg mole/hr)	Benzoic acid component mole fraction	Conversion (%)
10	0.1930	40.86
20	0.3521	81.87
30	0.3913	99.00
40	0.3620	99.00
50	0.3368	99.00

Table 4.7 shows that the conversion rate is increased linearly with the sulphuric acid molar flow rate. The benzoic acid component mole fraction and conversion rate is the highest at 30 kg mole/hr sulphuric acid molar flow rate.

4.3.2 Results of heat integration for acidification reactor

The range of optimization for conversion feed temperature was settled within $0^\circ C$ to $1000^\circ C$. After optimization, the purity and yield of benzoic acid were remained the same between $0^\circ C$ and $300^\circ C$. For temperature above $300^\circ C$, the component mole fraction and molar flow of benzoic acid decreased linearly with the temperature. This was because the boiling point of benzoic acid was at about $300^\circ C$. If the reactor temperature was exceeded $300^\circ C$, this could lower the component mole fraction and molar flow of benzoic acid since some of the benzoic acid may be vaporized at this temperature. Thus we have to control the reactor feed temperature to ensure that the reactor outlet temperature not exceeded $300^\circ C$. In this case, the optimum temperature chosen was at $200^\circ C$.

Table 4.8 Benzoic acid component mole fraction and molar flow at different temperature

Temperature (C)	Benzoic acid component mole fraction	Molar flow (kg mole/hr)
100	0.3952	123.6
200	0.3952	123.6
300	0.3952	123.6
400	0.0510	73.11
500	0.0007	69.23

From table 4.8, the benzoic acid component mole fraction and molar flow decreased when the temperature was above 300 $^{\circ}C$.

4.3.3 Comparison of optimization results

Below were the results of optimization after the reaction was completed and separated by the hydro cyclone.

Table 4.9 Results before and after optimization

	Before optimization	After optimization
Benzoic acid component mole fraction	0.4955	0.8785
Benzoic acid molar flow (kgmole/hr)	27.76	39.29
Sulphuric acid molar flow (kgmole/hr)	100	30
Temperature ($^{\circ}C$)	353	200

Table 4.9 shows the effluent results before and after the optimization. In this case, the reactor must operate at temperature below 300 $^{\circ}C$ and the suitable molar flow rate was 30 kg mole/hr of sulphuric acid in order to achieve high purity of benzoic acid.

4.3.3 Hydro cyclone efficiency

Other than varying the material molar flow and feed temperature for each reactor, the optimization of benzoic acid could also be done by varying the hydro cyclone efficiency.

The table below shows the results of purity and molar flow of benzoic acid for different efficiency.

Table 4.10 Benzoic acid purity at different hydro cyclone efficiency

Hydro cyclone efficiency (%)	Benzoic acid purity (%)
33	62.21
66	72.73
99	87.75

From table 4.10, higher efficiency of hydro cyclone would result in high purity but low molar flow of benzoic acid. Martin Rhodes (2008) found that high efficiency of hydro cyclone was characterized by small inlet and fluid outlet orifices. This would give high recoveries but at the same time would offer high resistance to the flow. On the other hands, low efficiency hydro cyclone had large inlet and fluid outlet orifices. This would results low recoveries and low resistance to the flow. Thus, high efficiency hydro cyclone gave higher purity but lower molar flow rate and low efficiency gave lower purity but high molar flow rate.

4.4 Optimization of chloroform and chlorine gas production

The chloroform and chlorine gas produced were by-products from this plant. The residue from the oxidation reactor was separated out and fed into a separator to remove the large amount of water. The inlet temperature must be maintained at $140^\circ C$ or above because if the temperature was below $140^\circ C$ the chlorine and chloroform will be washed out together with the water. After the water had washed out from the reactor, the remaining products would be fed into the distillation column to separate out the chlorine gas.

4.4.1 Optimization of chlorine by using distillation column specifications

The function of distillation column was to separate the chemical mixture based on their physical and chemical properties in order to get a better purity. The number of stages required for this distillation column was ten (10) and the feed stage location was plate number five (5) from the top. This number of stages and feed stage location was chose due to it could satisfy all the specifications made throughout the whole stimulation. The main purpose here was to separate the corrosive chlorine from the mixture. Two specifications were used in this distillate column, overhead products flow rate and reflux ratio.

For overhead products flow rate and reflux ratio specifications, specify it overhead product flow rate as 9 kg mole/hr and reflux ratio as six. At these specifications, the chlorine component mole fraction wass 0.9999 in vapour form while the chloroform component mole fraction was 0.6146 in liquid form. Although the overhead product molar flow was only 9 kg mole/hr out of 37.41 kg mole/hr, but it was already meet our requirement to separate the chlorine from the bottom liquids product.

On the other hands, the minimum reflux ration in this distillation column in order to separate the chlorine from the mixture is 6. As mentioned in section 4.1.3 before, the electricity is increased with increasing of reflux ratio. In this case, there is no different in chlorine and chloroform composition in overhead or bottom liquid products. Hence, use minimum reflux ratio in order to save the electricity cost. Below are the results of chlorine and chloroform composition in bottom liquid streams before and after separation by distillation column at the specifications state above.

Table 4.11 Chlorine and chloroform component mole fraction before and after enter the distillation column

	Before separation	After separation
Chlorine component mole fraction	0.5233	0.0002
Chloroform component mole fraction	0.3036	0.6146

Overhead products flow rate: 9 kg mole/hr Reflux ratio: 6

4.4.2 Optimization of chloroform by varying the separator inlet temperature

The bottom liquids product separated from the previous distillation column are now undergoes another separation by separator to obtain better purity of chloroform products. The optimization could be done by varying the inlet temperature of separator in order to get high purity of chloroform. The range of temperature would set between $0^\circ C$ and 100 C. From the table 4.12, the minimum temperature for the separation is at 60 C otherwise the chloroform will be washed out again together with the water. This was because the boiling point of the chloroform was at 60 C. If the temperature was below the boiling point all the chloroform would be in liquid form and if the temperature was beyond the boiling point the chloroform will be separated in vapour form and then undergoes liquefaction later to obtain the chloroform liquid. Besides, the chloroform component mole fraction was decreased with increasing temperature. Thus, the most suitable flow rate to obtain a better purity was at 60 C. Below are the results of chloroform component mole fraction and molar flow at different temperature.

Table 4.12 Chloroform component mole fraction and molar flow at different temperature

Temperature ($^{\circ}C$)	Chloroform component mole fraction	Chloroform molar flow rate (kg mole/hr)
-30	0.9439	0.00
0	0.9240	0.00
30	0.8780	0.00
60	0.8012	21.79
90	0.6146	28.41

4.5 Cost estimation

4.5.1 Total cost investment

a.) Equipment Cost (Seider et al, 2004)

1.) Distillation column (two distillation columns in the process)

Maximum allowable stress = S = 15000 psig (395.8 $^{\circ}F$) Weld efficiency = E =1

Number of trays = n =10 density = $\rho = 0.29\, lb/in^2$

Operating pressure = 275.4 psig Internal diameter = D_i = 4.921 ft

Design pressure = $P_d = \exp\{0.60608 + 0.91615 \ln P_0 + 0.0015655(\ln P_0)^2\}$ (4.1)

$= \exp\{0.60608 + 0.91615(\ln 275.4) + 0.0015655(\ln 275.4)^2\}$

= 331 psig

Height of the column = Head + (n-1)*tray spacing + bottoms (4.2)

= 4ft + (10-1)(1.804ft) + 10ft

= 30.236ft

Calculate the wall thickness,

$$t_p = \frac{P_d D_i}{2SE - 1.2P_d} = \frac{(331 psig)(4.921 ft \times 12in/_{1ft})}{2(15000 psig)(1) - 1.2(331 psig)} = 0.6600 in \qquad (4.3)$$

Since the minimum wall thickness for D $_i$ = 4.921 ft is 0.3125in, so we specify t $_p$ = 0.66in

Outer diameter = D_o = (0.66 in x 2) + (4.921 ft x 12 in/ 1ft) = 60.372 in

Consider wind load and earthquake for distillation column,

$$t_w = \frac{0.22(D_O + 18L^2)}{SD_O} = \frac{0.22\{60.372 in + 18(30.236 ft \times 12in/_{1ft})^2\}}{(15000\, lb/_{in^2})(60.372 in)^2} = 0.0095 in \qquad (4.4)$$

Required thickness to withstand internal pressure and wind load;

$t_R = 0.66in + 0.0095in = 0.6695in$

Average thickness = $t_V = \frac{t_R + t_P}{2} + C.A. = \frac{0.6695in + 0.66in}{2} + 0.125in = 0.7898in$ (4.5)

For increment of 1/8 in, specify t $_s$ = $0.875in$

Calculate the weight of shell and the two heads;

$$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho \qquad (4.6)$$

$$= \pi[(59.052in + 0.875in)(362.832in + 0.8\{59.052in\}][0.875in][0.29\, lb/_{in^2}]$$

= 19590 lb

Vertical tower for 9000 < W < 2500000 lb

$$C_V = \exp\{7.2756 + 0.18255(\ln W) + 0.02297(\ln W)^2\} \qquad (4.7)$$

$$= \exp\{7.2756 + 0.18255(\ln 19590) + 0.02297(\ln 19590)^2\}$$

= \$ 82675

Vertical tower for 3 < D $_i$ < 21ft and 12 < L < 40ft

$$C_{PL} = 300.9D_i^{0.63316}L^{0.80161} = 300.9(4.921ft)^{0.63316}(30.236ft)^{0.80161} = \$12688 \qquad (4.8)$$

Purchase cost: $C_P = F_M C_V + C_{PL} = (7.7)(\$82675) + \$12688 = \$649286$ (4.9)

For installed cost of sieve trays,

$$F_{TM} = 1.401 + 0.0724D_i = 1.401 + 0.0724(4.921ft) = 1.757 \qquad (4.10)$$

$$C_{BT} = 468\exp(0.1739D_i) = 468\exp[0.1739(4.921ft)] = \$1101 \qquad (4.11)$$

Given $F_{NT} = 1$ for $N_T < 20$, $F_{TT} = 1$ (assume sieve tray)

$$C_T = N_T F_{NT} F_{TT} F_{TM} C_{BT} = (10)(1)(1)(1.757)(\$1101) = \$19345 \tag{4.12}$$

Total purchase cost at CE index of 550 for 2 distillation columns

$$C_{TP} = (2)\left(\frac{550}{500}\right)(C_P + C_T) = (2)\left(\frac{550}{500}\right)(\$649286 + \$19345) = \$1470988 \tag{4.13}$$

$F_{BM} = 4.16$ for vertical pressure vessel,

Bare module cost: $C_{BM} = F_{BM}(C_{TP}) = (4.16)(\$1470988) = \$6119310$ (4.14)

2.) Condenser (two condensers in the process)

Given that $A_i = 72.18$ ft^2

*The materials of construction shell and tube is carbon steel and stainless steel

$$F_M = a + \left(\frac{A}{100}\right)^b = 9.6 + \left(\frac{72.18}{100}\right)^{0.06} = 10.58 \tag{4.15}$$

Assume $F_P = F_L = 1$

Assume floating head:

$$C_B = \exp\{11.667 - 0.8709(\ln A) + 0.09005(\ln A)^2\} \tag{4.16}$$

$$= \exp\ \{11.667 - 0.8709(\ln 72.18) + 0.09005(\ln 72.18)^2\}$$

$$= \$\ 14606$$

At cost index 550, the purchase cost for 2 distillation columns is:

$$C_P = (2)\left(\frac{550}{500}\right)F_P F_M F_L C_B = (2)\left(\frac{550}{500}\right)(1)(10.58)(1)(\$14606) = \$339970 \tag{4.17}$$

Bare module cost: $C_{BM} = F_{BM} C_P = (3.17)(\$339970) = \$1077705$

3.) Reboiler (three reboilers in the process)

Given that $A_i = 72.18$ ft^2

* The materials of construction shell and tube are tiatanium

Assume kettle vaporizer,

$$C_B = \exp\{11.967 - 0.8709 \ln A + 0.09005(\ln A)^2\} \tag{4.18}$$

$$= \exp\ \{11.967 - 0.8709(\ln 72.18) - 0.09005(\ln 72.18)^2\}$$

$$= \$\ 19716$$

Assume $F_P = F_L = 1$

$$F_M = a + \left(\frac{A}{100}\right)^b = 9.6 + \left(\frac{72.18}{100}\right)^{0.06} = 10.58$$

At cost index of 550, the purchase cost for 2 reboilers are

$$C_P = (2)\left(\frac{550}{500}\right) F_P F_M F_L C_B = (2)\left(\frac{550}{500}\right)(1)(10.58)(1)(\$19716) = \$458910$$

Bare module cost: $C_{BM} = F_{BM} C_P = (3.17)(\$458910) = \$1454745$

4.) Vertical pressure vessel (acidification reactor and oxidation reactor)

Given that the volume of vessel = V =1413 ft^3

Internal diameter = D$_i$=10.62 ft Length = L = 16 ft

Operating pressure = 275.4 psig Maximum allowable stress = S =15000psig

Design pressure =P$_d$= $\exp\{0.60608 + 0.91615 \ln P_0 + 0.0015655(\ln P_0)^2\}$

$$= \exp\{0.60608 + 0.91615 \ln 275.4 + 0.0015655(\ln 275.4)^2\}$$

$$= 331 \text{ psig}$$

Calculate wall thickness,

$$t_p = \frac{P_d D_i}{2SE - 1.2P_d} = \frac{(275.4\,psig)(10.62\,ft \times {}^{12in}\!/\!_{1ft})}{2(15000\,psig)(1) - 1.2(331\,psig)} = 1.186\,in$$

The minimum wall thickness for D$_i$ = 8.432ft is t$_p$ = 0.4375 in, so we specify $t_p = 1.186\,in$

Outer diameter = D_o = (1.186 in x 2) + (10.62 ft x 12 in/ 1ft) = 130 in

Consider wind load and earthquake for distillation column,

$$t_w = \frac{0.22(D_O + 18L^2)}{SD_O} = \frac{0.22\{130in + 18(16ft \times {}^{12in}\!/\!{}_{1ft})^2\}}{(15000\,{}^{lb}\!/\!{}_{in^2})(130in)^2} = 0..0006in$$

Required thickness to withstand internal pressure and wind load;

$$t_R = 1.1860in + 0.0006in = 1.1866in$$

Average thickness = $t_V = \frac{t_R + t_P}{2} + C.A. = \frac{1.1866in + 1.1860in}{2} + 0.125in = 1.3113in$

For increment of 1/8 in, specify $t_s = 1.375in$

Calculate the weight of shell and the two heads;

$$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho$$

$$= \pi[(127.44n + 1.375in)(192in + 0.8\{127.44in\}][1.375in][0.29\,{}^{lb}\!/\!{}_{in^2}]$$

= 47434 lb

Vertical vessels for 4200 < W < 1000000 lb

$$C_V = \exp\{7.0132 + 0.18255(\ln W) + 0.02297(\ln W)^2\} \qquad (4.19)$$

$$= \exp\{7.2756 + 0.18255(\ln 47434) + 0.02297(\ln 47434)^2\}$$

= \$ 147865

Vertical vessels for 3 < D_i < 21ft and 12 < L < 40ft

$$C_{PL} = 361.8D_i^{.0.73960}L^{0.70684} = 361.8(10.62ft)^{0.73960}(16ft)^{0.70684} = \$14740 \qquad (4.20)$$

*The materials of construction is titanium, $F_M = 7.7$

Purchase cost: $C_P = F_M C_V + C_{PL} = (7.7)(\$147865) + \$14740 = \$1153300$

At cost index of 550, the purchase cost for 3 vertical pressure vessels are

$$C_{TP} = (3)\left(\frac{550}{500}\right)C_P = (3)\left(\frac{550}{500}\right)(\$1153300) = \$3805890$$

Bare module cost: $C_{BM} = F_{BM}C_P = (4.16)(\$3805890) = \$15832502$

5.) Separator (vertical pressure vessel)

Given that the volume of vessel = V =706.3ft^3

Internal diameter = D$_i$ =8.432ft Length = L = 12.65ft

Design pressure =P$_d$ =10psig Maximum allowable stress = S =15000psig

Calculate wall thickness,

$$t_p = \frac{P_d D_i}{2SE - 1.2P_d} = \frac{(10psig)(8.432ft \times {}^{12in}/_{1ft})}{2(15000psig)(1) - 1.2(10psig)} = 0.0337in$$

The minimum wall thickness for D$_i$ = 8.432ft is t$_p$ = 0.4375 in

Outer diameter = D_o = (0.4375 in x 2) + (8.432 ft x 12 in/ 1ft) = 102 in

Consider wind load and earthquake for distillation column,

$$t_w = \frac{0.22(D_O + 18L^2)}{SD_O} = \frac{0.22(102in + 18)(12.65ft \times {}^{12in}/_{1ft})^2}{(15000\,{}^{lb}/_{in^2})(102in)^2} = 0.004in$$

Required thickness to withstand internal pressure and wind load;

$$t_R = 0.4375in + 0.004in = 0.4415in$$

Average thickness = $t_V = \frac{t_R + t_P}{2} + C.A. = \frac{0.4415in + 0.4375in}{2} + 0.125in = 0.5645in$

For increment of 1/8 in, specify t$_s$ = 0.625in

Calculate the weight of shell and the two heads;

$$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho$$

$$= \pi\left[(101.184in + 0.5in)(151.8in + 0.8\{101.184in\}\right]\left[0.625in\right]\left[0.163\,{}^{lb}/_{in^2}\right]$$

= 7584 lb

Vertical vessels for 4200 < W < 1000000 lb

$$C_V = \exp\left\{7.0132 + 0.18255(\ln W) + 0.02297(\ln W)^2\right\} \tag{4.21}$$

$$= \exp\left\{7.2756 + 0.18255(\ln 7584) + 0.02297(\ln 7584)^2\right\}$$

= \$ 35503

Vertical vessels for 3 < D$_i$ < 21ft and 12 < L < 40ft

$$C_{PL} = 361.8D_i^{0.73960}L^{0.70684} = 361.8(8.432ft)^{0.73960}(12.65ft)^{0.70684} = \$10527 \tag{4.22}$$

*The materials of construction is titanium, $F_M = 7.7$

Purchase cost: $C_P = F_M C_V + C_{PL} = (7.7)(\$35503) + \$10527 = \$283900$

6.) Horizontal pressure vessel (Packed bed reactor)

Given that the volume of vessel = V = 4237 ft^3

Internal diameter = D$_i$ = 23.4ft Length = L = 9.8ft

Design pressure =P$_d$ =10psig Maximum allowable stress = S =15000psig

Calculate wall thickness,

$$t_p = \frac{P_d D_i}{2SE - 1.2P_d} = \frac{(10psig)(12ft \times {}^{12in}\!/_{1ft})}{2(15000psig)(1) - 1.2(10psig)} = 0.0480in$$

The minimum wall thickness for D$_i$ = 12 ft is t$_p$ = 0.5 in

Since this is horizontal vessel and it is not subject to wind load and earthquake.

Required thickness to withstand internal pressure,

$t_V = t_p + C.A. = 0.5in + 0.125in = 0.625in$

For increments of 1/8 in, specify t_s =0.625 in

Calculate the weight of shell and the two heads;

$W = \pi(D_i + t_s)(L + 0.8D_i)t_s\rho$

$= \pi[(144in + 0.625in)(472.8in + 0.8\{144in\}][0.625in][0.29\, {}^{lb}\!/_{in^2}]$

= 48423 lb

Horizontal vessels for 1000 < W < 920000 lb

$C_V = \exp\{8.9552 - 0.2330(\ln W) + 0.04333(\ln W)^2\}$

$= \exp\{8.9552 + 0.18255(\ln 48423) + 0.02297(\ln 48423)^2\}$

= \$ 804227

Horizontal vessels for 3 < D$_i$ < 12ft

$$C_{PL} = 2005 D_i^{0.20294} = 2005(12ft)^{0.20294} = \$3320 \qquad (4.22)$$

*The materials of construction is titanium, $F_M = 7.7$

Purchase cost: $C_P = F_M C_V + C_{PL} = (7.7)(\$804227) + \$3320 = \$6195868$

At cost index of 550, the purchase cost is:

$$C_{TP} = \left(\frac{550}{500}\right)C_P = \left(\frac{550}{500}\right)(\$6195868) = \$6815455$$

Bare module cost: $C_{BM} = F_{BM}C_P = (3.05)(\$6815455) = \$20787138$

7.) Hydro cyclone (2 hydro cyclones in the process)

Given Q = 14.34 m^3/h or 63.14 gal/min

$$C_P = 240Q^{0.50} = 240(63.14)^{0.50} = \$1907 \tag{4.23}$$

At cost index of 550, the total purchase cost for 2 hydro cyclones is:

$$C_{TP} = \left(\frac{550}{500}\right)C_P = \left(\frac{550}{500}\right)(\$1907)(2) = \$4195$$

Bare module cost: $C_{BM} = F_{BM}C_{TP} = (1.39)(\$4195) = \$5831$

8.) Shell and tube heat exchanger (four heat exchangers in the process)

Given that total heat transfer area = A = 649.3 ft length of tube = L =20 ft

Shell side pressure = P =100psig

Assume the heat exchanger is fixed head:

$$C_B = \exp\{11.0545 - 0.9228(\ln A) + 0.09861(\ln A)^2\} \tag{4.24}$$

$$= \exp\{11.0545 - 0.9228(\ln 649.3) + 0.09861(\ln 649.3)^2\}$$

$$= \$\ 10036$$

*The materials for construction of shell/tube is titanium/titanium

$$F_M = a + \left(\frac{A}{100}\right)^b = 9.6 + \left(\frac{649.3}{100}\right)^{0.06} = 10.72$$

$F_L = 1$ for 20 ft tube length ;

$$F_P = 0.9803 + 0.018\left(\frac{P}{100}\right) + \left(\frac{P}{100}\right)^2 \tag{4.25}$$

$$= 0.9803 + 0.018\left(\frac{100}{100}\right) + \left(\frac{100}{100}\right)^2$$

$$= 1.9983$$

The total purchase cost at CE index 550 for 4 shell and tube heat exchanger

$$C_P = (4)\left(\frac{550}{500}\right)F_P F_M F_L C_B = (4)\left(\frac{550}{500}\right)(1.9983)(10.72)(1)(\$10036) = \$945951$$

Bare module cost: $C_{BM} = F_{BM}C_P = (3.17)(\$945951) = \$2998665$

9.) Mixer (three mixers in the process)

All mixer volume was specified at V = 270 ft^3

$$C_P = 3400V^{0.42} = 3400(270)^{0.42} = \$35699 \tag{4.26}$$

At cost index of 550, the total purchase cost for 3 mixers is

$$C_{TP} = (3)\left(\frac{550}{500}\right)C_P = (3)\left(\frac{550}{500}\right)(\$35699) = \$117807$$

10.) Storage tank (11 storage tank in the process)

Given the volume = V = 5283 gal

$$C_P = 18V^{0.72} = 18(5283)^{0.72} = \$8625 \tag{4.27}$$

At cost index of 550, the total purchase cost is

$$C_{TP} = \left(\frac{550}{500}\right)C_P = \left(\frac{550}{500}\right)(\$8625) = \$9488$$

11.) Centrifugal pump and electric motor

Given that the flow rate = 38.2 gal/min and pump head = 596 ft

Pump:

$$S = QH^{0.5} = (38.2GPM)(596ft)^{0.5} = 933 \tag{4.28}$$

$$C_B = \exp\left\{9.7171 - 0.6019[\ln S] - 0.0519[\ln S]^2\right\} \tag{4.29}$$

$$= \exp\left\{9.7171 - 0.6019[\ln 933] + 0.0519[\ln 933]^2\right\}$$

$$= \$\ 3066$$

$F_T = 2.5 \qquad\qquad F_M = 9.7$ (titanium)

$$C_P = F_T F_M C_B = (2.5)(9.7)(\$3066) = \$74351 \qquad (4.30)$$

Electric motor:

Given that the flow rate = 38.2 gpm and pump horsepower = 8.741 Hp

$$\eta_P = -0.316 + 0.24015(\ln Q) - 0.01199(\ln Q)^2 \qquad (4.31)$$

$$= -0.316 + 0.24015(\ln 38.2) - 0.01199(\ln 38.2)^2$$

$$= 0.4$$

$$\eta_M = 0.80 + 0.0319(\ln P_B) - 0.00182(\ln P_B)^2 \qquad (4.32)$$

$$= 0.80 + 0.0319(\ln 8.741) - 0.00182(\ln 8.741)^2$$

$$= 0.86$$

$$P_C = \frac{P_B}{\eta_M} = \frac{8.741Hp}{0.86} = 10.16Hp \qquad (4.33)$$

$$C_B = \exp\{5.8259 + 0.13141[\ln P_C] + 0.053255[\ln P_C]^2 + 0.028628[\ln P_C]^3 - 0.0035549[\ln P_C]^4\}$$

$$C_B = \exp\{5.8259 + 0.13141[\ln 10.16] + 0.053255[\ln 10.16]^2 + 0.028628[\ln 10.16]^3 - 0.0035549[\ln 10.16]^4\}$$

$$= \$\ 789$$

$$C_P = F_T C_B = (2.5)(\$789) = \$1973$$

At cost index of 550, the total purchase cost is

$$C_{TP} = \left(\frac{550}{500}\right)(\$74351 + \$1973) = \$83956$$

Bare module cost: $C_{BM} = F_{BM} C_{TP} = (3.30)(\$83956) = \$277055$

The bare module cost of equipment includes the direct cost and indirect cost of the equipment. The direct-cost items that are incurred in the construction of a plant, in addition to the cost of equipment are:

1. Equipment erection, including foundations and minor structural work.
2. Piping, including insulation and painting.

3. Electrical, power and lighting.
4. Instruments, local and control room.
5. Process buildings and structures.
6. Ancillary buildings, offices, laboratory buildings, workshops.
7. Storages, raw materials and finished product.
8. Utilities (Services), provision of plant for steam, water, air, firefighting services (if not cost separately).
9. Site preparation.

The indirect costs are considered as indirect expenses which are estimated by the equipment bare module cost. Different equipment has different bare module factor. The indirect cost included design and engineering cost, contractor fees, contingency allowance and cost of freight to deliver the equipment.

Table 4.13 bare module cost of equipment

Equipment	Quantity	Purchase cost ($)
Packed bed reactor (Horizontal pressure vessel)	1	20787138
Oxidation reactor (Vertical pressure vessel)	1	5277501
Acidification reactor (Vertical pressure vessel)	1	5277501
Distillation column (Vertical tower)	2	6119310
Separator 1 (Vertical pressure vessel)	1	5277501
Separator 2 (Vertical pressure vessel)	1	283900
Shell and tube heat exchanger	4	2998665
Condenser	2	1077705
Reboiler	2	1454745
Hydro cyclone	2	5831
Mixer	3	117807
Storage tank	11	104368
Centrifuges pump and electric motor	1	277055
Total	27	48089027

From table 4.13, we estimate that the total bare module cost (C_{TBM}) is \$ 48089027 or **US\$ 48 million**.

According to Seider et al (2010), to calculate the total capital investment cost, we still need to estimate the site developments cost, building cost and offsite facilities cost.

b.) Site development cost

For grass-roots plant, we assume 20% of total bare module cost

$$C_{site} = 0.2 \times C_{TBM} = 0.2 \times US\$48 million = US\$9.6 million$$

c.) Building cost

For grass-roots plant and non process building, we assume 20% of total bare module cost

$$C_{building} = 0.2 \times C_{TBM} = 0.2 \times US\$48 million = US\$9.6 million$$

d.) Offsite facilities cost

We assume 5% of the total bare module cost

$$C_{offsitefac ilities} = 0.05 \times US\$48 million = US\$2.4 million$$

e.) Contingency and contractor fees

The contingency and contractor fees are unanticipated costs incurred during the construction of plant. According to Guthrie(1969), the contingency and contractor fees are 18% of the summation of total bare module cost, civil cost and building cost.

$$C_{con} = 0.18 \times \left(C_{TBM} + C_{civil} + C_{building} + C_{offsitefac ilities}\right) \tag{4.34}$$

$$= 0.18 \times \left(US\$48 million + US\$9.6 million + US\$9.6 million + US\$2.4\right)$$

= US\$ 12.5 million

f.) Land prices

Land required = 10 acres = 435600 ft^2

$$\frac{US\$4}{ft^2} \times 435600\, ft^2 = US\$1.74 million$$

According to Guthrie (1969), the total permanent investment is calculated by using the equation below:

$$C_{TPI} = C_{TBM} + C_{Civil} + C_{Building} + C_{offsitefacilities} + C_{Land} + C_{Contractor} \tag{4.35}$$

= US$(48million + 9.6million + 9.6million + 2.4million + 1.74million + 12.5million)

= US$ 83.84million

g.) Working capital

We assume the working capital as 17.6% in order to cover the initial catalyst charges.

$$C_{TCI} = 0.176 \times C_{TPI} = 0.176 \times US\$83.84 million = US\$14.76 million$$

The total capital investment is calculated by the Guthrie method

$$C_{TCI} = C_{TPI} + C_{WC} = US\$83.84 million + US\$14.76 million = US\$98.6 million$$

Summary of total capital investment

Table 4.13 Total capital investment cost

Cost factor	Cost (US $ million)
Equipment and material i.) ISBL ii.) OSBL	43.2 4.8
Civil	9.6
Building	9.6
Engineering and construction	2.4
Freight and other expenses	-
Commissioning and start up	-
Sub total	69.6
Contingency and contractor fees	12.4
Sub total	82 (total depreciable capital C_{TDC})
Land (5 Acres)	1.74
Sub total	83.84 (total permanent investment C_{TPI})
Working capital	14.76
Grand total	**98.60 (total capital investment C_{TCI})**

4.5.2 Variable manufacturing cost

a.) Raw materials cost

Raw materials: benzene, acetic anhydride, sodium hypochlorite and sulfuric acid

1.) Benzene (ICIS, 2011)

Given that mass flow rate = 3905 kg/hr

$$C_{benzene} = \frac{\$1.16}{kg} \times \frac{3905kg}{hr} \times \frac{24hr}{1day} \times \frac{330day}{yr} \times \frac{yr}{37000MT} = \frac{US\$970}{MT}$$

2.) Acetic anhydride (ICIS, 2011)

Given that the mass flow rate = 5104 kg/hr

$$C_{Aceticanhydride} = \frac{\$1.15}{kg} \times \frac{5104}{hr} \times \frac{24hr}{day} \times \frac{330day}{yr} \times \frac{yr}{37000MT} = \frac{US\$1256}{MT}$$

3.) Sodium hypochlorite (ICIS, 2011)

Given that the volume flow rate = 8458 gal/hr

$$C_{NaOCl} = \frac{\$0.65}{gal} \times \frac{8458gal}{hr} \times \frac{24hr}{day} \times \frac{330day}{yr} \times \frac{yr}{37000MT} = \frac{US\$1177}{MT}$$

4.) Sulfuric acid (ICIS, 2011)

Given that the mass flow rate = 4904 kg/hr

$$C_{H2SO4} = \frac{\$0.11}{kg} \times \frac{2942kg}{hr} \times \frac{24hr}{day} \times \frac{330day}{yr} \times \frac{yr}{37000MT} = \frac{US\$69}{MT}$$

Total raw materials cost = $C_{benzene} + C_{aceticanhydride} + C_{NaOCl} + C_{H2SO4}$

= US$ (970 + 1256 + 1177 + 69)/MT

= US$ 3472/MT

b.) By products credit

1.) Acetic acid: (ICIS, 2011)

Given that the mass flow rate = 3020 kg/h

$$\frac{\$0.63}{kg} \times \frac{3020kg}{h} \times \frac{24h}{day} \times \frac{330days}{yr} \times \frac{yr}{37000MT} = \frac{US\$407}{MT}$$

2.) Sodium hydroxide: (ICIS, 2011)

Given that the mass flow rate = 5420 kg/h

$$\frac{\$0.32}{kg}\times\frac{5420kg}{h}\times\frac{24h}{day}\times\frac{330days}{yr}\times\frac{yr}{37000MT}=\frac{US\$371}{MT}$$

3.) Chloroform: (ICIS, 2011)

Given that the mass flow rate = 2153 kg/hr

$$\frac{\$0.70}{kg}\times\frac{2153kg}{hr}\times\frac{24hr}{day}\times\frac{330days}{yr}\times\frac{yr}{37000MT}=\frac{US\$323}{MT}$$

4.) Chlorine: (ICIS, 2011)

Given that the mass flow rate = 638.5 kg/hr

$$\frac{\$0.40}{kg}\times\frac{638.5kg}{hr}\times\frac{24hr}{day}\times\frac{330days}{yr}\times\frac{yr}{37000MT}=\frac{US\$55}{MT}$$

Total by-products credit:

US$ (407 + 371 + 323 + 55)/MT = US$1156/MT

c.)Utilities cost (Seider et al (2004). Product & process design principles: synthesis, analysis and evaluation)

1.) Steam

Given the total mass flow rate of steam = 17110 kg/hr + 360 kg/hr = 17470 kg/hr

$$\frac{\$6.60}{1000kg}\times 17470\frac{kg}{hr}\times\frac{24hr}{1day}\times\frac{330day}{1yr}\times\frac{yr}{37000MT}=\frac{US\$25}{MT}$$

2.) Cooling water

Given the total volume flow rate of cooling water = $18\frac{m^3}{hr}+18\frac{m^3}{hr}=36\frac{m^3}{hr}$

$$\frac{\$0.02}{m^3}\times 36\frac{m^3}{hr}\times\frac{24hr}{1day}\times\frac{330day}{1yr}\times\frac{yr}{37000MT}=\frac{US\$0.15}{MT}$$

3.) Electricity

Total electricity = 1767 kW + 590.3 kW + 510.7kW + 206.3 kW + 6.52kW = 3081 kW

$$\frac{\$0.06}{kW-hr}\times 3081kW\times\frac{24hr}{1day}\times\frac{330day}{1yr}\times\frac{yr}{37000MT}=\frac{US\$40}{MT}$$

Total utilities = US\$ (25 + 0.15 + 40)/MT = US\$ 65.15/MT

<u>Summary of variable manufacturing cost</u>

Table 4.14 Variable manufacturing cost

Cost factor	US $/MT
Raw materials	
i.) Benzene	970.0
ii.) Acetic anhydride	1256.0
iii.) Sodium hypochlorite	1177.0
iv.) Sulphuric acid	69.0
<u>Total</u>	<u>3472.0</u>
Utilities	
i.) Electricity	40.0
ii.) Steam	25.0
iii.) Cooling water	0.15
Total	<u>65.15</u>
Credit of by product	
i.) Sodium hydroxide	- 407.0
ii.) Chloroform	- 371.0
iii.) Acetic Acid	- 323.0
iv.) Chlorine gas	- 55.0
<u>Total</u>	<u>- 1156.0</u>
Total variable cost	**2381.15**

4.5.3 Manufacturing and general expenses

a.) Operation labor cost

Table 4.15 Labor cost

Position	Number	US$/month	Month total (US $)	Month/yr	Annual (US $)
Expatriate	1	12000	12000	12	144000
Managerial	1	8000	8000	12	96000
Executive	2	5000	10000	12	120000
Supervisory	3	3000	9000	12	108000
Technical	5	1800	9000	12	108000
Skilled	10	1200	12000	12	144000
Clerical	2	800	3200	12	38400
Others	2	500	1000	12	12000
Total	20	32300	64200		770400

Total labor cost per metric ton:

$$\frac{US\$770400}{yr} \times \frac{yr}{37000MT} = \frac{US\$21}{MT}$$

b.) Maintenance cost (Seider, et al (2004). Product & process design principles: sysnthesis, analysis and evaluation)

i.)Wages and benefit

We consider 4.5% of total depreciable cost (C_{TDC}) for fluid- solid handling process

MW & B = $C_{TDC} \times 0.045$ = US$ 82million x 0.045 = US$ 3.7million

ii.)Salaries and benefit

We consider 25% of MW & B

0.25 X US$ 3.7million = US$ 0.93million

iii.) Maintenance overhead

We consider 5% of MW & B

0.05 US$ 3.7million = US$ 0.19million

iv.) Materials overhead:

We consider 100% of MW & B

1 x US$ 3.7million = US$ 3.7 million

The total maintenance cost per metric ton:

$$\frac{US\$(3.7+0.93+0.19+3.7)million}{yr}\times\frac{yr}{37000MT}=\frac{US\$230}{MT}$$

c.) Plant overhead cost (Seider et al (2004). Product & process design principles: synthesis, analysis and evaluation)

We consider 22.8 % of the total cost of operating labor and maintenance per ton:

$$0.228\times\frac{US\$(21+230)}{MT}=\frac{US\$57}{MT}$$

d.) Tax and insurance cost

We consider 3% of total depreciable cost (C_{TDC})

US$ 82million x 0.03 = US$ 2.46million

Tax and insurance cost per metric ton:

$$\frac{US\$2.46million}{yr}\times\frac{yr}{37000MT}=\frac{US\$66.5}{MT}$$

e.) Total depreciable cost

According to Busche (1995), the depreciation cost is 8% of the total depreciation capital

$$C_{depreciation}=0.08\times C_{TDC}=0.08\times US\$82million=US\$6.56miliion$$

Depreciation cost per metric ton:

$$\frac{US\$6.56million}{yr} \times \frac{yr}{37000MT} = \frac{US\$177}{MT}$$

f.) General expenses

According to Busche (1995), the general expenses included selling cost, research cost, administration cost and financing interest. Below is the percentage contributed by each section:

Sales price of ethylene = US$4100/MT

Selling cost = 3% of sales = $0.03 \times {US\$4100}/{MT} = {US\$123}/{MT}$

Research cost = 0.5% of sales = $0.005 \times {US\$4100}/{MT} = {US\$20.5}/{MT}$

Administration cost = 2% of sales = $0.02 \times {US\$4100}/{MT} = {US\$82}/{MT}$

Financing interest = 1.25% of sales = $0.0125 \times {US\$4100}/{MT} = {US\$51.25}/{MT}$

Total cost of general expenses = US$276.75/MT

Summary of manufacturing and general expenses

Table 4.16 Manufacturing and general expenses cost

Cost factor	US$/MT
Manufacturing expenses	
i.) Operation labor costs	21.0
ii.) Maintenance costs	230.0
iii.) Plant overhead cost	57.0
iv.) Depreciation cost	66.5
v.) Tax and insurance cost	177.0
Total manufacturing expenses	551.5
General expenses	
i.) Selling costs	123.0
ii.) Research costs	20.5
iii.) Administration costs	82.0
iv.) Financing interest	51.25
Total general expenses	276.75
Total fixed cost (Manufacturing expenses + general expenses)	828.25

4.5.4 Summary of benzoic acid annual production cost

Table 4.17 Annual production cost

1.) Variable Manufacturing Cost	**US$/MT**
a.) Raw materials	
i.) Benzene	970.0
ii.) Acetic anhydride	1256.0
iii.) Sodium hypochlorite	1177.0
iv.) Sulphuric acid	69.0
Total raw materials	3472.0
b.) Utilities	
i.) Electricity	40.0
ii.) Steam	25.0
iii.) Cooling water	0.15
Total utilities	65.15
c.) By-products credit	
i.) Acetic acid	- 407.0
ii.) Sodium hydroxide	- 371.0
iii.) Chloroform	- 323.0
iv.) Chlorine	- 55.0
Total by-products credit	-1156.0
Total variable manufacturing cost	**2381.15**
2.) Manufacturing Expenses	
a.) Operation labour costs	21
b.) Maintenance costs	230
c.) Plant overhead costs	57
d.) Depreciation costs	177
e.) Tax and insurance cost	66.5
Total Manufacturing Expenses	**551.5**
3.) General Expenses	
a.) Selling costs	123
b.) Research costs	20.5
c.) Administration costs	82
d.) Finance interest	51.25
Total General Expenses	**276.75**
Total fixed cost (Manufacturing Expenses + General Expense)	**828.25**

Annual production cost of benzoic acid =US$ (2381.15 + 828.25)/MT = **US$ 3209.4/MT**

4.6 Breakeven point calculation

Fixed cost per ton = US$ 828.25/MT
Benzoic acid production capacity = 37 KTA
Total fixed cost = US$ 30645250/yr

Benzoic acid sales price per ton = US$ 4100/MT
Variable Costs per ton = US$ 2381.15/MT

a.) Contribution margin per ton = Benzoic acid sales price per ton – Variable costs per ton
= US$ 4100/MT – US$ 2381.15/MT
= US$ 1718.85/MT

b.) Sales volume = Total fixed costs/Contribution margin per ton

$$= \frac{US\$30645250 \big/ yr}{US\$1718.85 \big/ MT}$$

= 17829MT/yr
= 48.85 MT/day

Breakeven point would be:

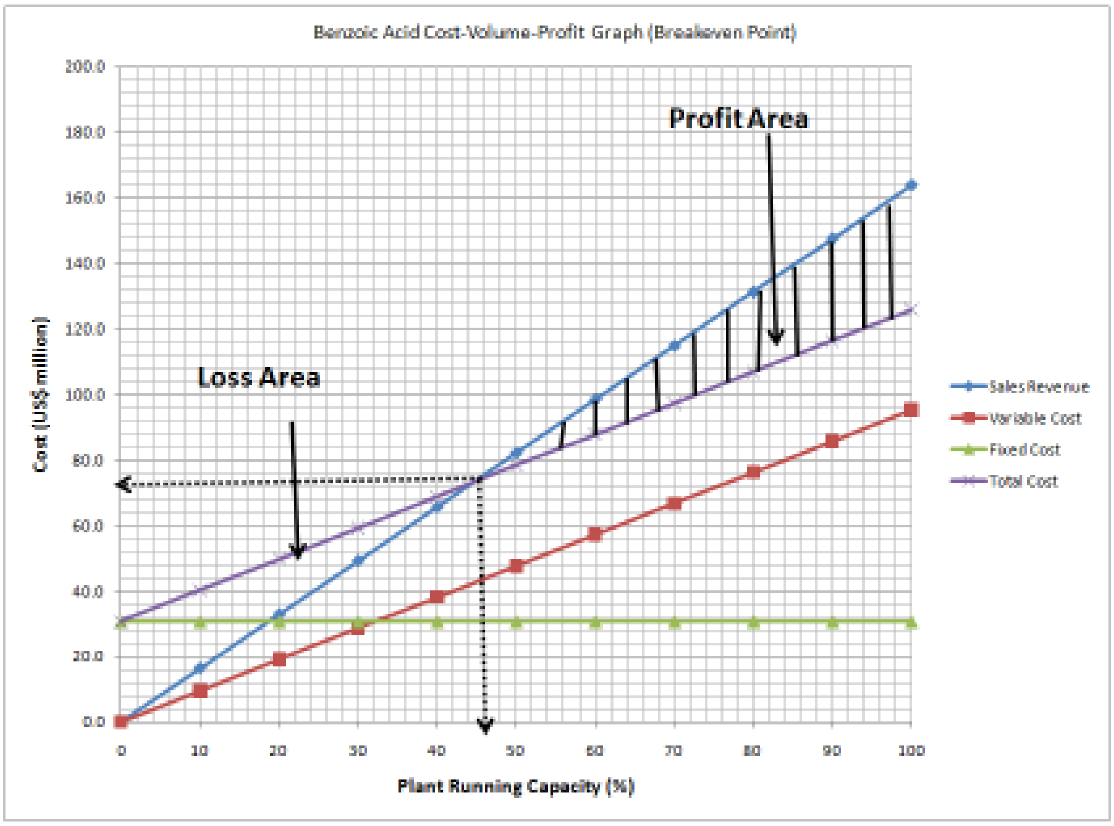
c.) Sales revenue = Sales volume x Sales price
= 17829MT/yr x US$4100/MT
= US$ 73 million/yr

d.) Output capacity = (Sales volume/ Production capacity)*100%

$$= \frac{17829MT \big/ yr}{37000MT \big/ yr} \times 100\%$$

= 48.2%

Figure 4.1 Benzoic Acid Cost Volume Profit Graph (Breakeven point)



From figure 4.1, the non-shade area is loss area while the shade area is profit area. This also indicates that the output capacity is 48% and the cost revenue per year was US$ 72 million.

e.) Contribution margin ratio = (Sales price – Variable costs)/Sales price

$$= \frac{\left(US\$4100\big/_{MT} - US\$2381.15\big/_{MT}\right)}{US\$4100\big/_{MT}} \times 100\%$$

$$= 42\%$$

4.7 Profit calculation

Benzoic acid sales price = US$ 4100/MT

Annual cost production = US$ 2381.15/MT

a.) Net profit = Sales price – Cost of production

= (US$ 4100/MT) – (US$3209.4/MT)

= US$ 890.6/MT

b.) Sales profit = (Net profit/Sales price) x 100%

$$= \frac{US\$890.6/MT}{US\$4100/MT} \times 100\%$$

$$= 21.72\%$$

4.8 Return of investment calculation

Total capital investment = US$ 98.6 million

Net profit value = US$ 890.6/MT or US$ 32.95 million/yr

a.) Return On Investment = (Net profit value/Total capital investment) x 100%

$$= \frac{US\$32.95 million/yr}{US\$98,60 million} \times 100\%$$

= 33.42%

b.) Return period = Total capital investment/Net profit value

$$= \frac{US\$98.60 million}{US\$32.95 million/yr}$$

= 3 years

4.9 Summary of benzoic acid project economics analysis review

Table 4.18 Benzoic acid economics analysis

Plant capacity	40 KTA
Operating rate	90.4
Benzoic acid price	$ 4100/MT
Benzoic acid production capacity	37 KTA
Fixed investment cost	$ 98.60 million
Variable cost	$ 2381.15/MT
Fixed cost	$ 828.25/MT
Annual production cost	$ 3209.4/MT
Contribution margin ratio	42%
Net profit	$ 890.6/MT
Sales profit	21.72%
Return on investment (ROI)	33.42%
Return period	3 years
Breakeven point (sales revenue)	US$ 73 million/yr
Breakeven point (output capacity)	48.2%

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The main results and feedback of this research to the simulation of benzoic acid production are the following.

i.) The simulation of benzoic acid production plant by using acetic anhydride and benzene as raw materials and sodium hypochlorite as an oxidizing reagents was successfully developed using ASPEN HYSYS 3.2

ii.) The optimum molar flow rate for benzene and sodium hypochlorite molar flow rate were 50 kg mole/hr and 1200 kg mole/hr respectively at acetic anhydride basis molar flow rate 50 kg mole/hr.

iii.) The optimum temperature for acylation of benzene is at room temperature while for oxidation of acetophenone by Clorox(sodium hypochlorite) is at $700^\circ C$.

iv.) The optimum hydro cyclone efficiency is at 99%

v.) For the optimum parameters above, the purity of benzoic acid achieved is 89% and the mass flow rate is 4681 kg/hr.

vi.) The annual profit of benzoic acid is US$ 890.6/MT and the return period of this plant is 3 years.

vii.) Strong oxidizing agent sodium hypochlorite is more economical and environmental friendly if compared to potassium permanganate (IV).

Potassium permanganate (IV) releasing heavy metal ions which are dangerous to the environment and costly. Sodium hypochlorite was cheap and the only hazardous chemical produced was chlorine which could be sold as by-products.

5.2 Recommendations

In the future works, it is recommended to study the following aspects:

i.) Water management

Water was one of the component flows out from the reaction that has been simulated. The reuse of the water as cooling or hot water that removed from the distillation column and separator can be done. This can save the water utility cost and thus maximize our profit.

ii.) Energy integration basis

It can be done by maximize the recovery of waste heat from various portion of the reactor. Waste process heat is utilized to generate steam needed in the process. This is more economic.

iii.) Reactor arrangement

Reactor in series can increase the conversion and also the yield of the products. The volume needed to achieve a maximum conversion for reactor in series is smaller than the volume of single reactor.

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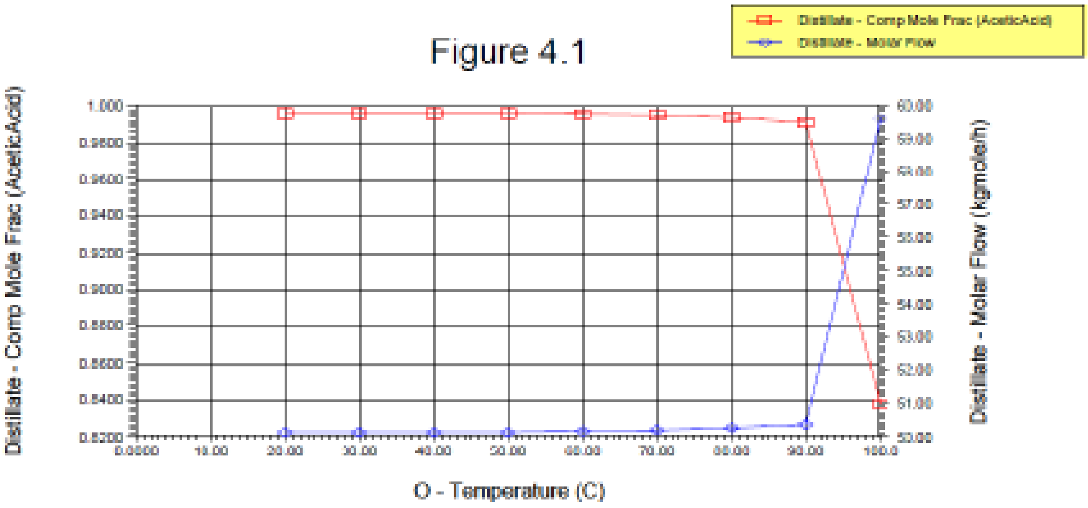
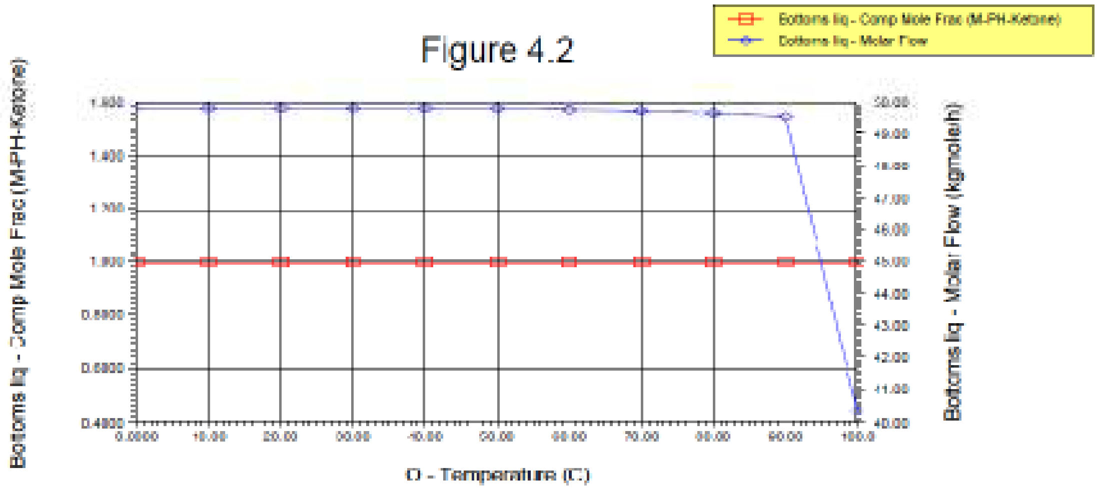
APPENDIX A

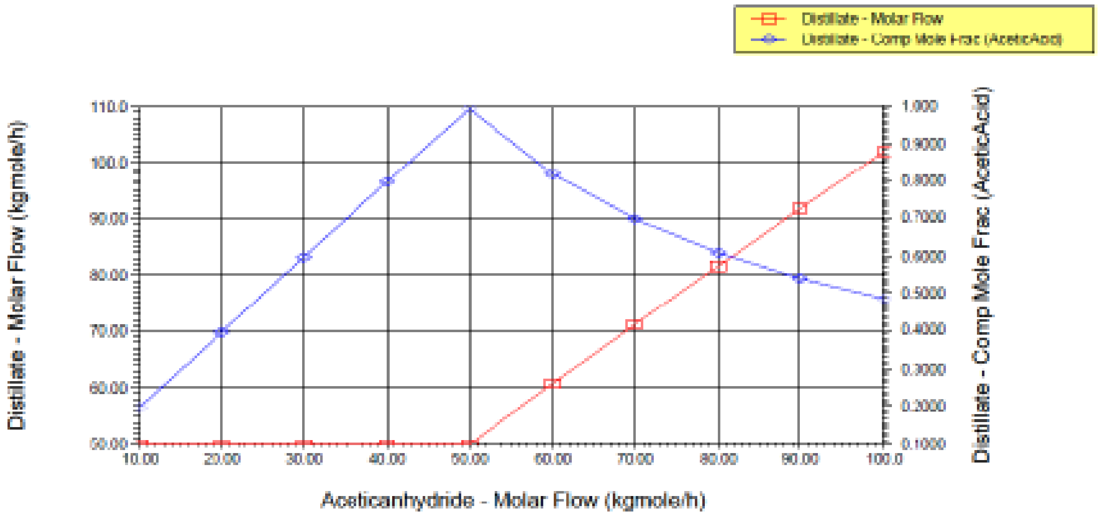
A.1 Distillate molar flow and acetic acid component mole fraction Vs Temperature



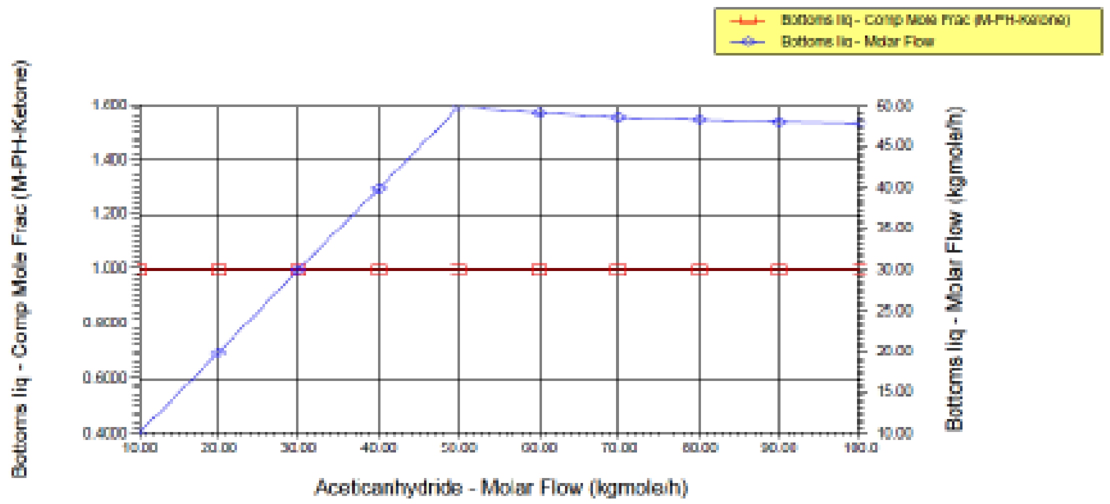
A.2 Bottoms liq molar flow and acetophenone component mole fraction VS temperature



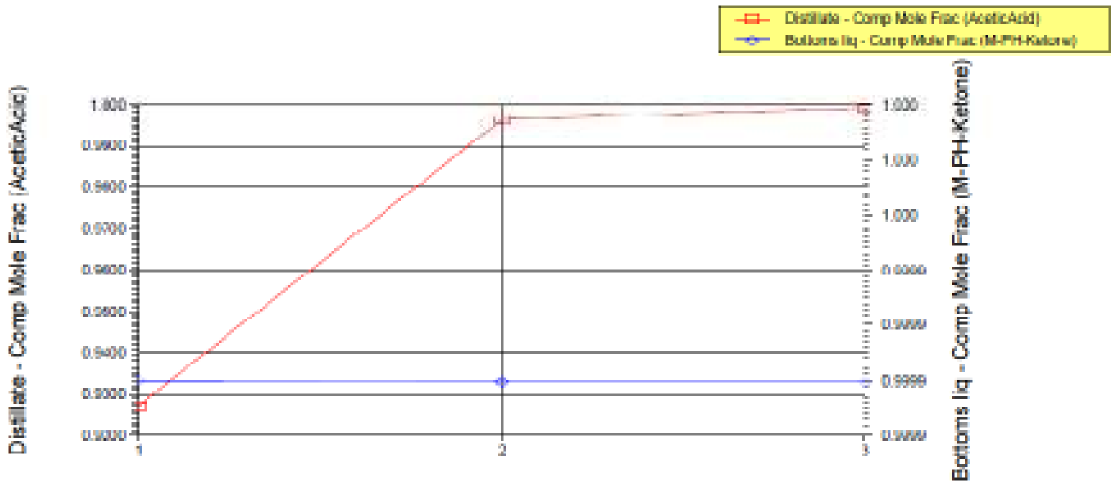
A.3 Distillate molar flow and acetic acid component mole fraction VS Acetic anhydride molar flow



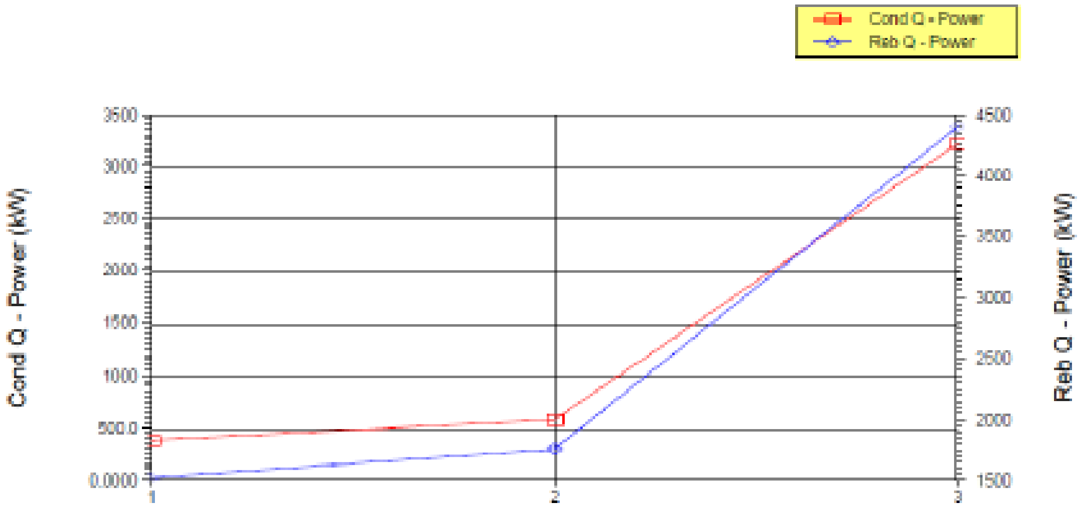
A.4 Bottoms liq molar flow and acetophenone component mole fraction VS Acetic anhydride molar flow



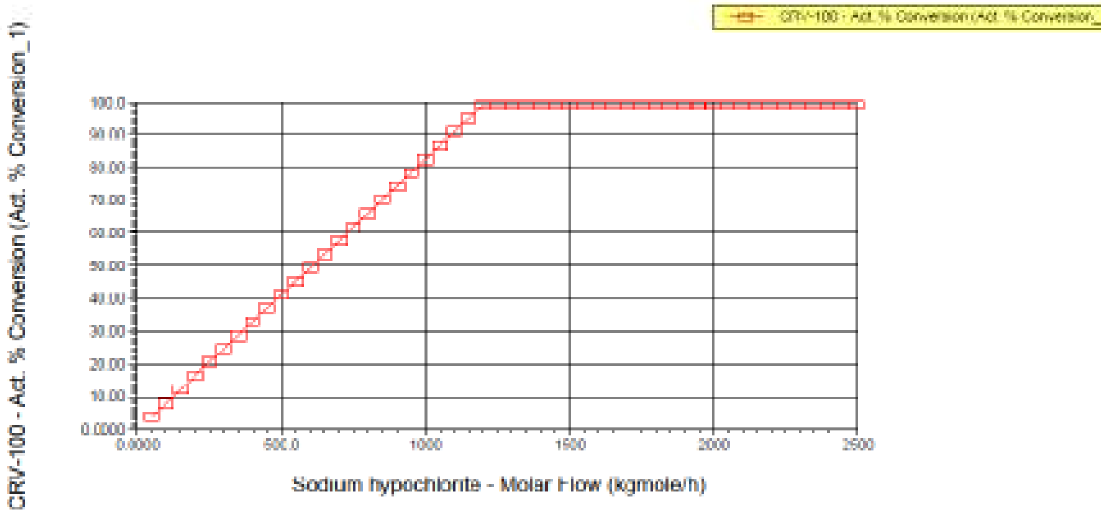
A.5 Distillate acetic acid and bottoms liq acetophenone component mole fraction VS reflux ratio



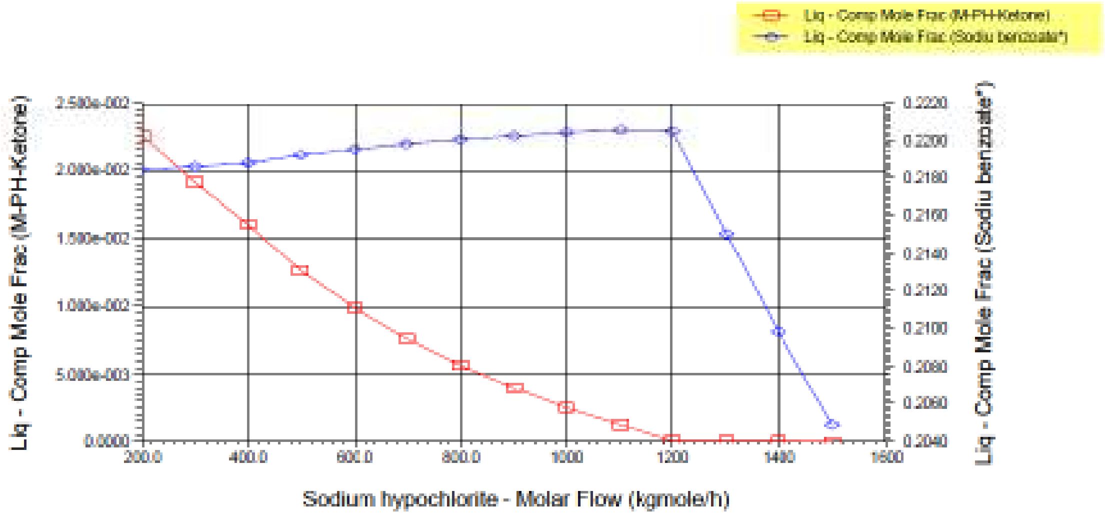
A.6 Condenser and reboiler power VS reflux ratio



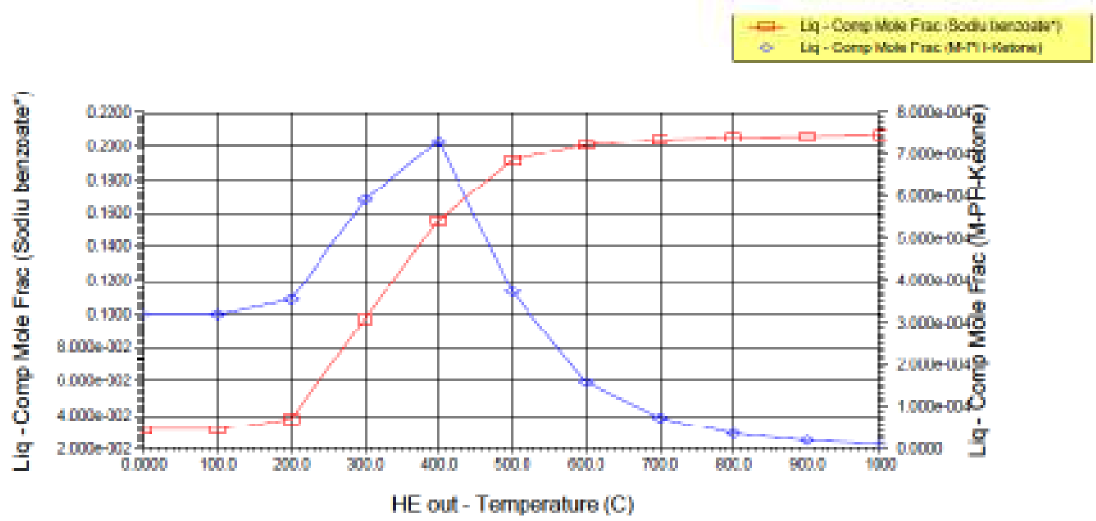
A.7 Oxidation reactor conversion rate VS Sodium hypochlorite molar flow



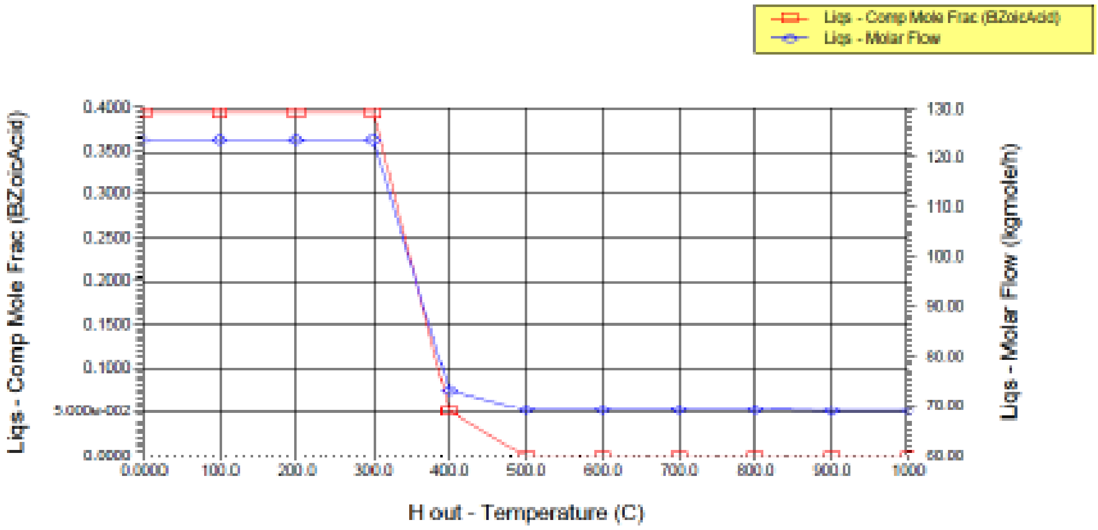
A.8 Liq streams acetophenone and sodium benzoate component mole fraction VS Sodium hypochlorite molar flow



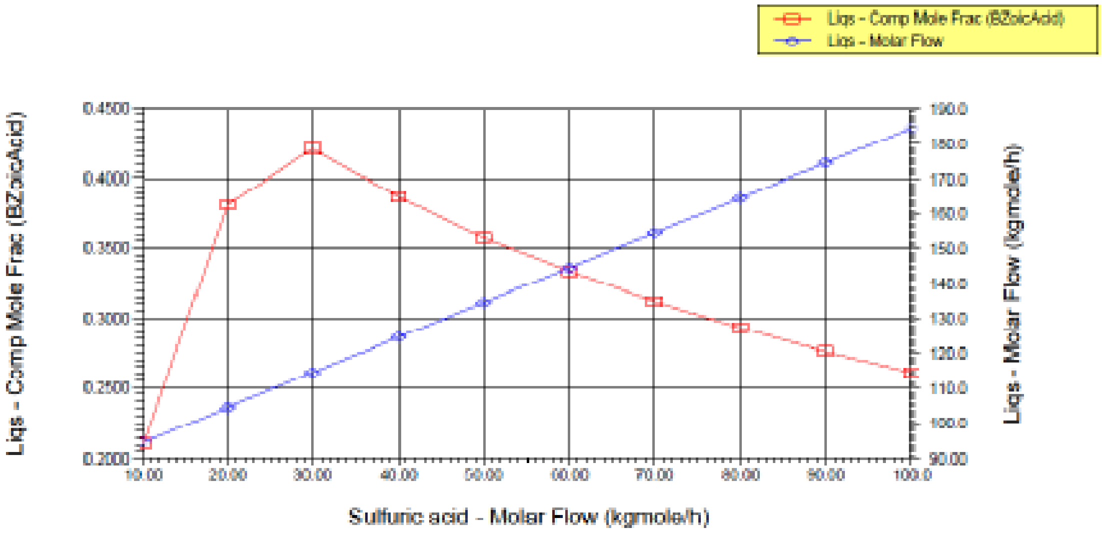
A.9 Liq streams acetophenone and sodium benzoate component mole fraction VS oxidation reactor inlet temperature



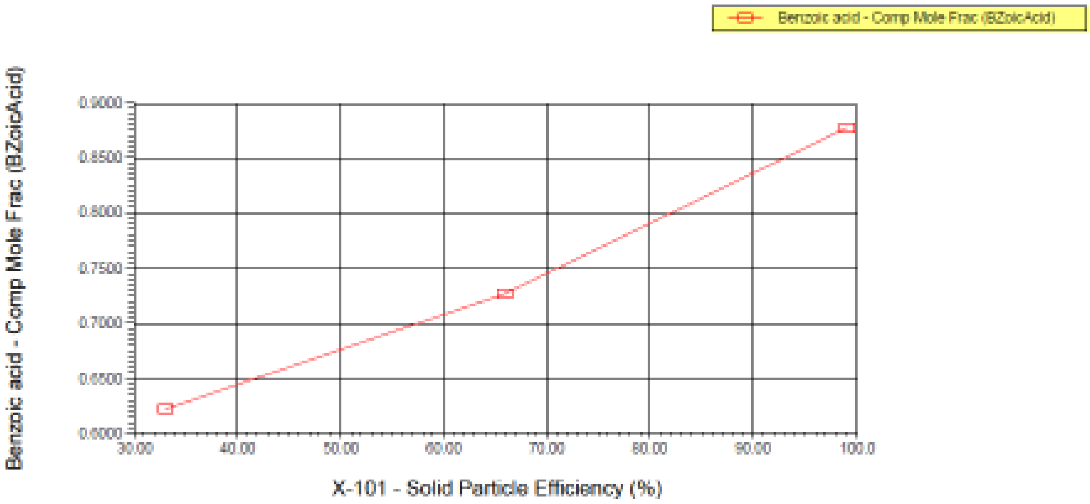
A.10 Liqs streams molar flow and benzoic acid component mole fraction VS acidification inlet temperature



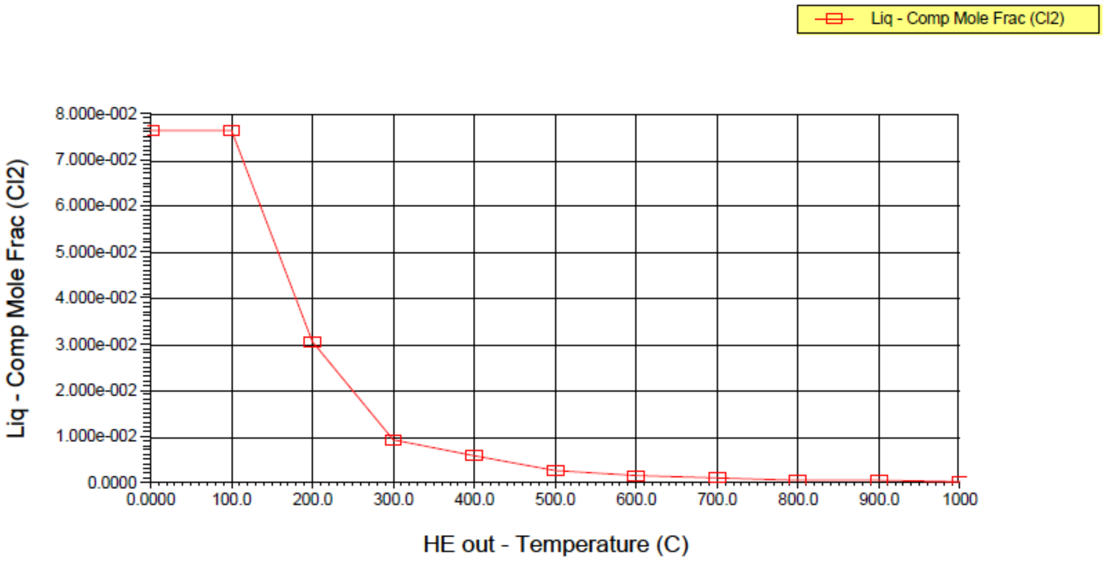
A.11 Liqs streams molar flow and benzoic acid component mole fraction VS sulphuric acid molar flow



A.12 Benzoic acid component mole fraction VS Hydrocyclone 2 separation efficiency



A.13 Liq streams chlorine component mole fraction VS separator 1 inlet temperature



A.14 Chlorofrom molar flow and component mole fraction VS separator 2 inlet temperature