CHAPTER I

INTRODUCTION

1.1 Background

Paraxylene also called 1.4 dimethyl benzene is classified into aromatic compounds. Paraxylene is an intermediate product which is used widely in chemical industry. This material can be further processed into several kinds of end products. Paraxylene is primarily used as raw material in the manufacture of terephthalic acid (TPA) and dimethyl-terephthalate (DMT). TPA and DMT are used to manufacture polyethylene terephthalate (PET) saturated polyester polymers.

Growth of synthetic fiber for textile and downstream, will increase paraxylene demand each year. The establishment of paraxylene plant as upstream petrochemical industry has good prospects because product can be further processed into products that are needed in daily life.

Indonesia import in oil, gas and petrochemical sector reached US $32 billion. Import is done to meet demand for crude oil, fuel oil, naphtha, ethylene, propylene, polyethylene, polypropylene, paraxylene,benzene (http://bisnis. tempo. co/read/news/2012/12/14/090448291/2016-indonesia-bakal-kebanjiran-produk-petrokimia FRIDAY, DECEMBER 14, 2012 | 19:22 pm)

Petrochemical sector needs a new plant to produce paraxylene (petrochemical products used as raw materials of the textile industry) to reach capacity of 500,000 ton per year. Current capacity in country reached 7,750 tons /year. Demand of paraxylene is estimated will reach 1.25 million tons (http://www.kemenperin.go.id/artikel/2944/Investasi-Sektor-Petrokimia-Butuh-Dana-US$-6,8-Miliar accesd on 10/08/2015)

Establishment of paraxylene plant will provide benefits such as:

1. Existence of paraxylene plant will saves foreign exchange by reducing amount of paraxylene imports and reduce dependence on other country

2. Establishment of paraxylene plant will create jobs and absorb labors.
3. Stimulating growth of new industries that use paraxylene as raw material.
4. Improving quality of human resources through transfer of technology.

1.2 Design capacity

Determination of paraxylene plant capacity can be viewed from several considerations, among others:

1.2.1. Projection of Paraxylene Demand in Indonesia

Paraxylene demand in Indonesia is still largely imported from abroad. National average paraxylene import demand per year is increase, as shown in Table 1.1. This is related to developments of industrial sectors that use paraxylene as raw material.

By using the least squares method y = bx + a, it can be estimated paraxylene import demand (kg/year) . It can be estimate demand of paraxylene in 2020 will reach 1,008,946,107 kg/year .

1.2.2 Capacity of Existing Plant

In determining capacity plant, it can be seen from capacity of plant that has been established. Paraxylene plant in Indonesia which has been operated is Pertamina UP IV Cilacap with production capacity 270,000 ton/year and started operating since 1990.

Due to above consideration , it is possible to build this plant with capacity 400,000 ton/year to cover domestic demand in Indonesia.

1.3. Site Selection

There are several factor that must be considered to determine location of plant establishment, in order to be technically and economically profitable. Paraxylene plant is planned to be established in cilegon industrial area , with following considerations :

Primary factor.

a. Source of raw materials

b. Marketing
c. The provision of electricity and fuel
d. labor

Secondary factor.

a. Transportation
b. Water supply
c. State of society
d. Characteristics of the location

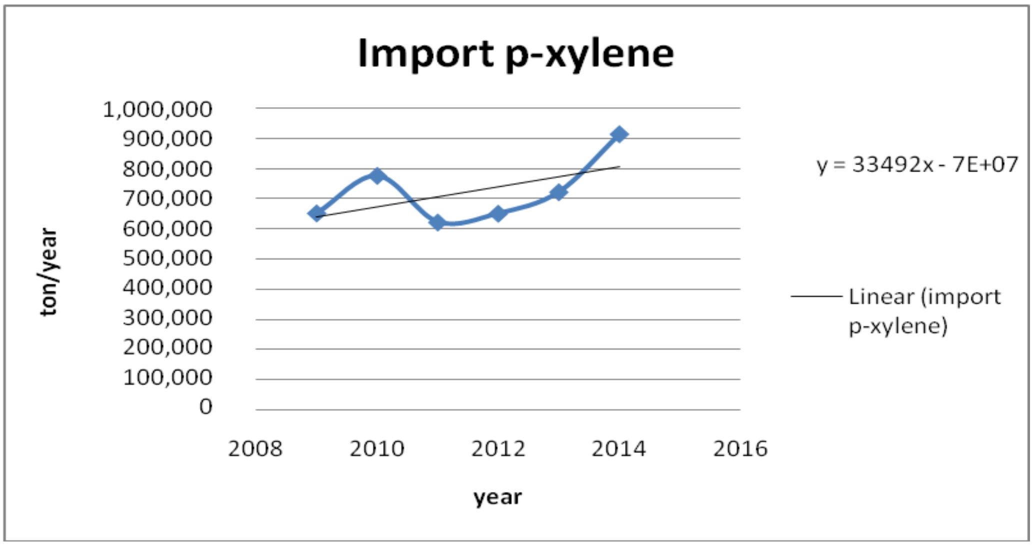


Figure 1.1 Import Paraxylene ton/year

Based considerations above, paraxylene plant is planned to be built in the industrial area of Cilegon, Banten. The reason for choosing these locations among others :

a. Raw material

Cilegon has very strategic location because it close to Port Merak, which catalyst is obtained from import. It also has great transportation facilities to transport raw material toluene that is obtained from PT candra Asih. While hydrogen gas can be obtained by inline through underground pipes from PT. ALIndo which is located in Cilegon.

b. Marketing

Marketing is one of the important factor to decisive feasibility level in establishing plant. Marketing of paraxylene product is emphasized to meet domestic demand. As is known, in Cilegon there are PT Amoco Mitsui Indonesia, PT. Polyprima Karyareksa, and PT. Mitsubishi Chemical Indonesia which is use paraxylene as raw material to produce purified terephthalic acid (PTA).

c. Transportation

Transportation is needed to transport materials, market products and others. Therefore, roadways and seaports are highly required. Transportation in Cilegon industrial area are highway and seaport which make easier for retrieval of raw materials and marketing products to other regions.

d. Utilities

Water, electricity and fuel are needed for production process to run well. Availability of water, electricity,energy and other are already adequate because this area has been established many large-scale factories.

e. Labor

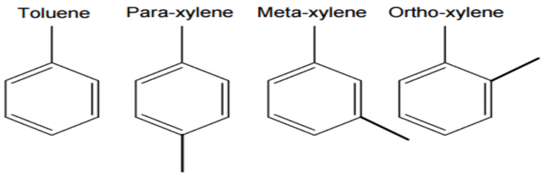
Labor demand can be met from Merak and surroundings as well as area is densely populated so that supply labor is not a problem.

f. Possibility of Industrial Area Development

Establishement in industrial area is allows to obtain ease permit in handling and development of plant site in future.

1.4 Literature review

Para-xylene (PX), Ethylbenzene (EB), ortho-xylene (OX) and meta-xylene (MX) are often present together in a typical industrial C_8 aromatic product stream from a chemical plant or a refinery. Among the four C_8 aromatic compounds, all having the same molecular formula C_8H_{IO}. Terms mixed xylene describes a mixture containing tthe three xylene isomers and usually EB. Paraxylene is obtained from separation of its isomers (OX and MX).



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(kirk othmer vol 4.)

1.4.1 Kinds of Process

Two principal methods for producing xylenes are catalytic reforming and toluene disproportination

a. Mixed xylene Production via Reforming

In catalytic reforming, a low octane naptha cut (typically a straight run or hydrocracked naphta) is converted into high octane aromatics, including benzene, toluene and mixed xylenes. Aromatic are separated from reformate using a solvent such as diethylene glycol and sulfolane and then stripped from the solvent.distilation is then used to separate BTX (benzene, tolunen, xylene) into its components. The amount of xylenes contained in catalytic reformate depends on the fraction and type of crude oil, the reformer operating condition and the catalyst used. Typically ranging from 18 to 33 vol% of the reformate. (kirk othmer vol 4)

b. Xylenes production via toluene transalkylation and disproportionation.

The toluene disproportionation is defined as the reaction of 2 mol of tolunene to produced 1 mol of xylene and 1 mol of benzene . toluene transalkyation is defined as the reaction of toluenen with c9 or higher aromatics to produce xylenes .

Other species that are also present in the feed, such as ethyl benzene and methylbenzenes will also undergo transalkyllation reactions. The reaction tend to approach an equlibrium that depends on the operating conditions. (kirk othmer vol 4.)

There are several commercial processes that produce xylenes via disproportionation or transalkylation. These include : UOP’s Tatoray and PX-Plus, ARCO’s Xylenes Plus, and Mobil’s MTDP and STDP.

1. UOP's Tatoray and PX-Plus

In this process, toluene or a mixture of toluene and C9+ aromatics are reacted to form primariy xylenes and benzene. The catalyst is designet TA-4. It has high per pass conversion and good stability. Yields to xylenes are reported to be over 97%. The pelleted catalyst is used in fixed bed reactor in the presence of hydrogen. Typical operating condition are : 350-530°C, 1-5 Mpa (10-50atm) and H2/hydrocarbon ratio of 5-12:1. Toluene per pass conversion can be increased by increasing pressure or temperature, although this also reduces yield and increses the rate of catalyst deactivation.

2. Xylenes Plus

Xylene Plus also converts toluene with or without C_9^+ aromatic. Feed that have been comercially used include catalytic reformate and hydrotreated pygas. Catalyst is non noble metal. Hydrogen is not required for any facet (start-up, operation, catalyst regeneration) of the process.,and thus operating pressure is relatively low. Reported that 30% per pass conversion result in highest possible yield of xylenes with minimal feedstock loss to gas or coke. EB production is close to zero.

3. Mobil's MTDP and STDP.

Mobil has developed several TDP processes. In the 1970s Mobil developed their LTD (Low Temperature Disproportionation) process. This was a liquid-phase process which used what described as siliceous zeolitic catalysts. Hydrogen was not required in this process. The initial reactor temperature was 127°C and was raised as the catalyst deactivated to maintain toluene conversion. Catalyst was regenarated after temperature reached about 315°C.

In the mid 1970s, Mobil introduced their MTDP process. This is vapor phase process that uses ZSM-5 type zeolites. The process operates at 48 wt% toluene per pass conversion with a near equlibrium PX selectivity of 24% in the xylenes product. Typical operating conditions are inlet temperature of 390-495°C, H_2 partial pressure of 4.1 Mpa, H_2/hydrocarbon molar ratio of 4, and liquid hourly space velocity (LHSV) = 1.0-2.0/h. EB production was about 3 wt% of feed.

In the late 190s, Mobil commercialized the MSTDP (Mobil Selective Toluene Disproportionation) proces. In MSTDP, PX selectivity can be boosted to 80-90% at toluene conversion of about 25-30%. The significantly higher than equilibrium yield of PX is obtained by precoking the catalyst in the reactor. As coking occurs, the toluene conversion progressively drops from 60% to about 20-30%, whereas the PX selectivity increases from 24% to about 80-90%. It means that the subsequent crystallization or adsorption PX recovery facilities can be significantly smaler. Typical operating condition are 400-470°C, 2.0-3.4 Mpa, WHSV= 2-4/h, H_2/hydrocarbon molar ratio of 1-3.1.

In the design chosen as selective toluene disproportonation because :

- selectivity of paraxylene is higher at low conversion . It cause easier and cheeper in purification

1.4.2 Uses of Product

a. Main Product (Paraxylene)

PX has largest commercial market. PX is used primarily for manufacturing purified terephthalic acid (PTA) and terephthalate esters such as dimethyl terephthalate (DMT), Which are used for making various polymers such as poly(ethylene terephthalate), or PET, poly(propylene terephthalate), or PPT, and poly(buteneterephthalate), or PBT. (US 6,878,855 B2, 2005)

Paraxylene is also used as a protective layer, as a solvent in resin. Example for coating with p-xylene are brushing enamel, paint for ships, coating equipment vessel, mix paints, paper coatings, textile coatings, refractory materials, waterproof materials. Type of resin which is usually dissolved in paraxylene are natural resins, alkyd, phenol pure, vinyl, polystearine, acrylic resin, Maleic resins, ester of gum. Paraxylene is used as an extender in rubber synthesis and used in photographic color printing, lithography metallic ink, for printing silk and linen oil.Description of use of paraxylene in a variety of industries listed in Table 1.1

b. Side Product (Benzene)

Benzene is widely used in industry as solvent in extraction and distillation operations purposes. Raw materials for manufacture ,organic chemical compounds or intermediate of products and commercial products, for example: styrene, cumene cyclohexane.

1.4.3 Physical and Chemical Properties of Raw materials and Products

a. Raw Maaterial

1. Toluene

- Physical Properties

  Molecular formula : C_7H_8
  Phase at T,P room : liquid
  Molecular weight : 92.14 g/mol
  Normal melting point : -95°C
  Normal boiling point : 111°C
  Density (25°C) : 0.866 g/mL
  Critcal Temperature : 320.8°C
  Critcal Pressure : 41.6 atm

(http://www.chemicalbook.com)

Table 1.1. Use of Paraxylene in Industry

No.	Type Usage	Usage Process
1.	raw material PTA	PTA intermediate products
2.	Solvent evaporation	Added on substances that will be vaporized so that process faster
3.	Xylidine	Nitration of xylene compounds into nitroxylene and converted into xylidine
4.	Synsis of Dacron	Paraxylene oxidized fibers mixed methanol and ethyl glycol
5.	Petroleum	aviation component and a mixture of gasoline at a price high antiknock
6.	Emulsifier of fungicide and insecticides	Dissolution toxaphene, hexachlorobenzene
7.	Solvent	Solvents resin natural resin, phenol pure, vinyl, styrene, acrylic resins, resin Maleic, rubber, melamine, phenol, phenol formaldehyde
8.	Dyes	Used for fotography, lithography, print silk, batik, etc.
9.	Adhesives	Blended with syntic rubber, neoprene
10.	Hidrotoping agent	sulfonation reaction to distinction solubility in separation isomer
11.	Material Removal	spotting polisher for dry drying
12.	Xylenols	Sulfonation followed by desulfonasi as material burning caustic.

- Chemical propeties

Toluene is a derivative of benzene, which has chemical properties:

1. If chlorine gas is passed into a boiling toluene with aid UV rays of H atoms in group will be replaced by atoms methyl Cl.

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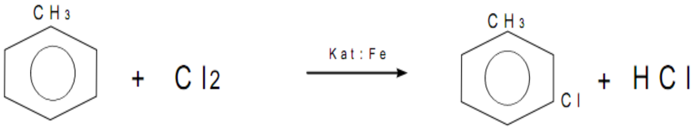
2. If chlorine gas is passed at room temperature with aid of an iron catalyst, and hydrogen atom in cycle will be replaced by a Cl atom.



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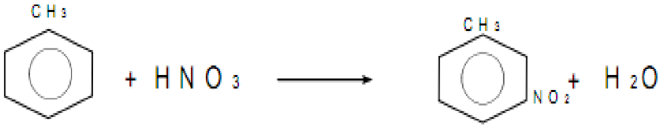
3. If reacted with nitric acid and sulfuric acid will be formed nitrotoluene.



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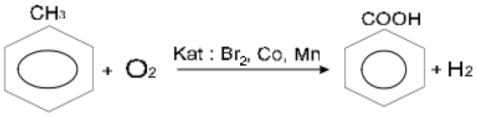
4. In oxidation reaction with oxygen and with aid of a catalyst bromine, cobalt, manganese .and produces benzoic acid.



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2. Hydrogen

- Physical properties :

Phase at T and P room : gas

Molecular weight : 2.001 g/mol

Normal boiling Point	: -252.7°C
Normal melting point	: -259.1°C
Density (25°C)	: 0.0352 g/mL
Crtical Temperature	: -239.9°C
Critcal Pressure	: 12.83 atm
Viscosity (25°C)	: 0.013 cp

(http://www.chemicalbook.com)

- Chemical Properties:
  1. Reaction of hydrogen with a halogen acid forming hidrohalogenida.
     $H_2 + X_2 \rightarrow 2\,HX$
  2. Reaction between hydrogen and oxygen to form water.
     $H + \frac{1}{2} O_2 \rightarrow H_2O$
  3. Reaction between hydrogen and carbon to form methane.
     $2H_2 + C \rightarrow CH_4$
  4. Reaction between hydrogen with nitrogen to form ammonia.
     $3H_2 + N_2 \rightarrow 2NH_3$
  5. Reaction between hydrogen with metals to form metal hybrid.
     $H_2 + N \rightarrow NH_2$
  6. Reaction between hydrogen and metal oxides to form metal and water.
     $H_{2\,+}\ MO \rightarrow M + H_2O$

b. Product

1. Paraxylene (Product)

- Physical Properties

Molecular formula	: C_8H_{10}
Molecular weight	: 106.17 g/mol
Normal melting point	: 12-13°C
Normal boiling point	: 138°C
Density (25°C)	: 0.861 g/mL

Critical Temperature : 3,433.05°C
Critical Pressure : 34 atm

(http://www.chemicalbook.com)

- Chemical properties

Chemical reaction that xylenes participate in includes :

1. Migration of methyl Groups

   Reaction that involved migration of methyl groups are isomerization, disporportionation and dealkylation. Interconversion of three xylenes isomers via isomerization is catalyzed by acids. Acids can be liquid or solids. Transalkylation is also catalyzed by acids but requires more severe condition than isomerization.

2. Reactions of methyl groups.

   Reactions include oxidation,poly condensation and ammoxidation. PX can be oxidized to both terephathalic acid from polyesters. Oxidation of OX yileds phtalic anhydride, which is used in production of esters. MX is oxidized to isophthalic acid, which is also converted to esters and eventually used in plasticizers and resins.

   In study of slow combustion of three xylenes it was observed that OX is much more reactive towards oxygen than MX and PX. Under identical conditions OX was approximately ten times as reactive as its isomers.

3. Reaction of aromatic ring

   Reaction of aromatic ring of C_8 aromatic isomers are generally electropilic subtitution reaction. All of classical electrophilic substitution reactions are possible, but in most instances are little practiceal significance. Nuclear chloronation rates of polymethylbenzenes have been studied. Higher degree subtitution cause higher rate of chorination.

   As most electrophilic reaction, ability to stabilize positive charge generated by initial addition strongly affects rates. MX react faster than OX and PX becaue these methyl groups work in conjunction to stabilize charge on one carbon. Sulfonation was used to separate MX from C_8

aromatic isomers. MX react most rapidly to form sulfonic acid which is remain in aqueous phase. Sulfonation reaction is reversible, and MX can be regenerated

4. Complex formation

   All of four C_8 aromatic isomers have strong tendency to form several different types of complex. Complexes with electrophilic agent are utilized in xylenes separation. Formation of HF-BF3-MX complex is basis of Mitsubishi Gas-Chemical Company (MGCC) commercial process for MX recovery, discussed herein. Equimolar complexes of MX and HBr (mp-77°C).

c. Side Product

1. Benzene (Side Product)

- Physical Properties

  Molecular formula : C_6H_6
  Molecular weight : 78.11 g/mol
  Normal Melting point : 5.5°C
  Normal Boiling point : 80°C
  Density (25°C) : 0.874 g/mL

(http://www.chemicalbook.com)

- Chemical Properties:
  1. Substitution

     Under appropriate conditions, one or more hydrogen atoms in benzene may be replaced by halogen atoms or nitro, sulfonic more.
  2. Oxidation

     Benzene can be oxidized to products that is different. With a catalyst such as permanganate or chromic acid, benzene oxidized into water and CO_2.

3. Reduction

   Benzene can be reduced to cyclohexane. At room temperature, benzene may be hydrogenated with a nickel catalyst, hydrogenation speed will be tripled with a rise in temperature from 20°C to 50°C.

4. Pyrolysis

   If benzene is passed through a red hot iron tube or in high temperature resulting diphenyl compound with a vanadium catalyst. At temperatures above 750°C benzene decomposes into carbon and hydrogen.

5. Halogenated

   Product substitution or addition halaogenasi obtained with benzene. Reacted with Br_2 and Cl_2 obtained benzene chloride and benzene bromide with $FeCl_3$ catalyst. Klorobenzene obtained by reacting at a temperature of 30-50°C with molybdenum chloride catalyst.

6. Nitration

   When benzene is reacted with a mixture of nitric acid and mercury obtained palmiat nitrophenol.

7. Alkylation

   Alkylation of benzene such as ethyl benzene, and cumene produced commercial by reacting benzene with ethylene or propylene vapor and liquid. Catalyst used is $AlCl_3$,BF_3, zeolite.