CHAPTER I
INTRODUCTION

1.1. Background

In the industrial and free trade era, it is necessary to set up an industry that can provide great benefit to the development of industry in Indonesia. One type of these industries include industrial of titanium dioxide (TiO_2). Based on statistical data, Indonesia is still importing titanium dioxide from China, Australia, Japan, USA, etc. (BPS, 2015).

Titanium is a very important element for several industrial applications, being one of the ninth most abundant elements in the Earth’s crust (0.63% wt.) (Gazquez, 2014). Titanium is known to have similar strength with steel but 45% lighter and 65% heavier than the weight of aluminum, but twice as strong as aluminum. Nearly 90% of titanium is consumed in the world in a form of titanium dioxide (TiO_2).

It is the brightest white pigment with the highest opacity of any commercial product, and is used to impart whiteness and opacity to paints, plastics, paper and in many other smaller applications. TiO_2 can also improve the durability of coatings, paper laminate and plastic items. Because of its clean tone and opacifying properties, TiO_2 is widely used in pastel and colored finishes as well as whites. Around 60% is used in paints or coatings, 20% in plastics, 12% in paper and 8% in a wide range of smaller applications.

The three common phases of titanium dioxide are rutile, anatase, and brookite. Rutile is the most stable form of titanium dioxide. Anatase and brookite are stable at normal temperatures but slowly convert to rutile upon heating to temperature above 600 and 550˚C, respectively shows in Figure 1.1. The rutile form is the most stable at higher temperature and low pressure.
In the industry, the more frequently used pigment is pigment rutile, rutile TiO$_2$ has an advantage because it has a refractive index, tinting strength, and oil absorption greater than anatase TiO$_2$ (Gazquez, 2014).

Table 1.1 Comparison the characteristic of rutile and anatase (Subagja, 2013)

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Rutile</th>
<th>Anatase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index</td>
<td>2.76</td>
<td>2.52</td>
</tr>
<tr>
<td>Tinting strength</td>
<td>1750-1850</td>
<td>1250</td>
</tr>
<tr>
<td>Oil absorption</td>
<td>16-36</td>
<td>16-26</td>
</tr>
</tbody>
</table>

Table 1.1 shows that rutile is better to be used as a pigment than anatase. Refractive index suggests that the rutile has high adhesion, while value of tinting strength suggests that the rutile has a better ability to change the color of another pigment, and oil absorption demonstrated high ability to absorb oil rutile greater than anatase.

According to the Ministry of Industry, Indonesia has a large enough source of ilmenite. It is about 40,000,000 tons, and from the data shown by the Ministry of Energy and Mineral Resources, shows Bangka Belitung province as one of the largest owners of ilmenite.
Based on statistical data, it is estimated the needs of titanium dioxide in Indonesia will increase in the coming years. A solution to overcome the needs of titanium dioxide in Indonesia, one way out is to produce TiO$_2$ by utilizing the mineral ilmenite which is widely available in Bangka Island with ilmenite content of up to 90%. These considerations that underlie the titanium dioxide plant set up in Indonesia.

1.2. Design Capacity

In determining the design capacity of the plant by looking at minimum capacity or equal to the capacity of existing plants. In addition, the determination of capacity must also approach the domestic demand for the product produced. Determining the capacity of the product is based on the following considerations:

1.2.1. Titanium Dioxide Consumption

Domestic needs of titanium dioxide most is still imported from abroad. Imports of titanium dioxide comes mostly from China as a manufacturer of titanium dioxide in the world. Titanium dioxide import developments in Indonesia can be seen in Table 1.2 below.

<table>
<thead>
<tr>
<th>Years</th>
<th>Consumption (tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>46,706.1100</td>
</tr>
<tr>
<td>2012</td>
<td>51,581.2400</td>
</tr>
<tr>
<td>2013</td>
<td>50,381.6330</td>
</tr>
<tr>
<td>2014</td>
<td>53,456.7600</td>
</tr>
</tbody>
</table>
When do a linear approach, will be obtained by the equation

\[ y = 1905.2x + 45768 \]  

By equation (1) estimated in 2020 that Indonesia needs of titanium dioxide 57,199,2000 tons.

1.2.2. Raw Materials Consumption

Availability of raw materials greatly affect the continuity of the process of a plant. The raw material consists of Ilmenite obtained from waste of PT. Timah Tbk. that’s located on the Belitung Island. Availability of raw materials reached 12,000 tons/month and chlorine gas (\( \text{Cl}_2 \)) imported from China and coke as a reduction agent.

1.2.3. Minimum Capacity

Minimum capacity of feasible plant can be known from the capacity of existing plant. Table 1.3 shows titanium dioxide plant in the world and its capacity.
Table 1.3 Titanium Dioxide Companies in the World and Its Production Capacity

<table>
<thead>
<tr>
<th>Company</th>
<th>Production Capacity (tons/ year)</th>
<th>Location</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kronos Worldwide Inc.</td>
<td>40,000</td>
<td>Cranbury, New Jersey</td>
<td><a href="http://kronostio2.com/en/component/content/category/17-manufacturing-facilities">http://kronostio2.com/en/component/content/category/17-manufacturing-facilities</a></td>
</tr>
<tr>
<td>Nanjing Titanium Dioxide Chemical Co., Ltd.</td>
<td>80,000</td>
<td>Jiangsu, China</td>
<td><a href="http://www.nthcl.com/ecompany.html">www.nthcl.com/ecompany.html</a></td>
</tr>
<tr>
<td>Zhejiang Ningbo Xinfu Titanium Dioxide Co., Ltd.</td>
<td>100,000</td>
<td>Shanghai, China</td>
<td><a href="http://xinfutio2.com/en/aboutus.html">http://xinfutio2.com/en/aboutus.html</a></td>
</tr>
<tr>
<td>Shandong Dongja Group, Henan Billions Chemicals Co., Ltd.</td>
<td>160,000</td>
<td>China</td>
<td><a href="http://www.dongjianggroup.com/about.aspx">www.dongjianggroup.com/about.aspx</a></td>
</tr>
<tr>
<td>CNNC Hua Yuan Titanium Dioxide Co., Ltd.</td>
<td>200,000</td>
<td>Shanghai, China</td>
<td><a href="http://www.sinotio2.com/node/37">www.sinotio2.com/node/37</a></td>
</tr>
<tr>
<td>Tronox Inc.</td>
<td>225,000</td>
<td>Mississippi, USA</td>
<td><a href="http://www.tronox.com/electrolytics-and-specialty-chemicals/operations/hamilton-mississippi-u-s/">http://www.tronox.com/electrolytics-and-specialty-chemicals/operations/hamilton-mississippi-u-s/</a></td>
</tr>
</tbody>
</table>

From the results of data processing and review of titanium dioxide production capacity of the plant that has been operating and market absorption capability, so it will be built the titanium dioxide plant using the chloride process with a capacity of 55,000 tons/year. The capacity of this plant has had feasibility evidenced by the plant with a capacity which has been established and the plant will start operating in 2020.
1.3. Plant Location

The plant will be built in East Belitung Area, Bangka Belitung. The factors that influence in considerations of plant location in Belitung Island, among others:

1.3.1. Raw Materials

Raw materials from titanium dioxide (TiO₂) plant are ilmenite derived from residual of tin mining around Belitung Island and chlorine gas imported from China.

1.3.2. Marketing

To reduce transportation costs and ease in selling the product, then marketing factors need to be taken into account in the selection of the plant location. Titanium dioxide is a finished product and is often used as an additive for ceramics, paints, and cosmetics industry. This product is planned to be distributed for domestic needs, the location of the plant is located close to the port so as to reduce the cost of transporting the product from plant to the carrier. On the Belitung Island, there is the Manggar Port are being traffic import-export trade on the Belitung Island.

1.3.3. Utility

Utilities are required involves the need of electricity, water, and fuel. Electricity needs can be met from the Steam Turbine Generator that rebuilt itself. Water requirements can be obtained from the river near the plant that is Manggar River.

1.3.4. Labor

The large number of workers of productive age who have not come to pass, because it was for manpower can be obtained easily from the surrounding community. Based on statistical data, amounted to 60.71% of Belitung community included in the working age population and the remaining 39.29% is not a resident of the labor force (school, taking care of the household and others).
1.3.5. Transportation and Telecommunication

Transportation is one of the factors that need to be taken into account in selecting the plant location, because of the existence of a good transportation will help the smooth working of the plant in the distribution and communication. In this case the transportation tend to be easy because of the location of the port and the Java-Sumatra highway, so that the distribution of the product is easy to do.

1.4. Literature Review

1.4.1. Production Process Description

There are two processes of titanium dioxide manufacturer, namely:

a) Chloride Process (EPA, 2001)

The chloride process begins with the conversion of high-grade ilmenite into titanium tetrachloride. This step occurs in a fluidized bed chlorinator in the presence of chlorine gas at a temperature of approximately 900°C. Coke also is added as a reductant. The volatile TiCl$_4$, including FeCl$_3$, CO, N$_2$, Cl$_2$, exit the chlorinator as overhead vapor. And residue of impurities, the unreacted coke and ore solids are removed from the gas stream and from the bottom of the chlorinator. The gaseous product stream is purified to separate the titanium tetrachloride from other metal chloride impurities using condensation. Vent gases from the chlorinator are absorbed in the Absorber to absorb Cl$_2$ content taken in the gas stream. The purified TiCl$_4$ is then oxidized to TiO$_2$, driving off chlorine gas, which is recycled to the chlorinator. The pure TiO$_2$ is slurred and sent to finishing process.

b) Sulfate Process (EPA, 2001)

The sulfate process starts with dried and milled slag TiO$_2$ being dissolved in sulfuric acid and water in a digester. This produces a titanyl sulfate liquor. From the digester the titanyl sulfate liquor goes to a clarification tank where the undissolved ore and solids are allowed to
settle. The titanium liquor then is concentrated and hydrolyzed to titanium dioxide hydrate. The titanium dioxide hydrate precipitates from the ferrous sulfate and sulfuric acid is separated through filtration. After filtration the hydrated titanium dioxide slurry is sent to a calciner, where the titanium dioxide crystals grow to their final crystalline size and residual water and \( \text{H}_2\text{SO}_4 \) are removed. The dried titanium dioxide is sent to pigments finishing. This finishing phase involves any required milling and or chemical treatment, such as surface coating with silica or alumina.

**Table 1.4 Comparison of Titanium Dioxide Manufacture Process**

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Sulfate Process</th>
<th>Chloride Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Conditions</td>
<td>Reactor 1: ( P = 3.5 \text{ atm} ) ( T = 473.15 \text{ K} ) Reactor 2: ( P = 1 \text{ atm} ) ( T = 363.15 \text{ K} )</td>
<td>Reactor 1: ( P = 1 \text{ atm} ) ( T = 1173.15 \text{ K} ) Reactor 2: ( P = 1 \text{ atm} ) ( T = 1273.15 \text{ K} )</td>
</tr>
<tr>
<td>Waste</td>
<td>FeSO(_4) formed in large quantities can cause environmental problems</td>
<td>No form of waste in large quantities</td>
</tr>
<tr>
<td>Product Quality</td>
<td>Produce titanium dioxide low quality of anatase.</td>
<td>Produce titanium dioxide high quality of rutile. Rutile is the most stable oxide titania.</td>
</tr>
</tbody>
</table>

Based on the above considerations, titanium dioxide plant will use the chloride process for titanium dioxide which would be produced in the form of rutile that to be used as a pigment in the paint, ceramics, and fiber industry and others.

**1.4.2. Uses of Titanium Dioxide**

Titanium dioxide is used as a white pigment (in paints, plastics, rubber, and paper), industrial ceramics, fiber, cosmetics, and also used as catalysts and photocatalysts.
1.4.3. Physical and Chemical Properties of Raw Materials and Products

a) Raw Materials

1. Ilmenite (Perry, 1997)

   Chemical composition (Subagja, 2013):
   - TiO$_2$ : 38.30%
   - Fe$_2$O$_3$ : 49.44%
   - Impurities : 12.26%, which consist of:
     - SiO$_2$ : 1.76%
     - Al$_2$O$_3$ : 1.78%
     - MnO : 2.00%
     - MgO : 1.44%
     - CaO : 0.08%
     - K$_2$O : 0.03%
     - P$_2$O$_5$ : 0.17%
     - Cr$_2$O$_3$ : 2.66%
     - SnO$_2$ : 1.16%

1.1. Titanium Dioxide

   Physical Properties (Perry, 1997):
   - Formula : TiO$_2$
   - Formula weight, g/mol : 79.90
   - Specific gravity : 4.26
   - Melting point at 1 atm, °C : 1640
   - Boiling point at 1 atm, °C : 3000
   - Formation heat, kcal/mol : -225.0
   - Gibbs energy, kcal/mol : -221.9

   Chemical properties (Kirk and Othmer, 1981):
   - Not flammable
   - Not corrosive
   - Insoluble in water
1.2. Iron (III) Oxide

Physical Properties (Perry, 1997):
- Formula : Fe$_2$O$_3$
- Formula weight, g/mol : 159.70
- Specific gravity : 5.12
- Melting point at 1 atm, °C : 1560
- Boiling point at 1 atm, °C : 3600
- Formation heat, kcal/mol : -198.5
- Gibbs energy, kcal/mol : -179.1

Chemical properties (Kirk and Othmer, 1981):
- Solution in acid
- Insoluble in water and organic solvents

2. Chlorine

Physical Properties (Perry, 1997):
- Formula : Cl$_2$
- Formula weight, g/mol : 70.91
- Specific gravity : 2.49
- Melting point at 1 atm, °C : -101.6
- Boiling point at 1 atm, °C : -34.6
- Formation heat, kcal/mol : 0
- Gibbs energy, kcal/mol : 0

Chemical properties (Kirk and Othmer, 1981):
- Not flammable
- Soluble in water
- Easy react with other compounds
- Toxic
Preliminary Design of Titanium Dioxide Plant from Ilmenite
Capacity of 55,000 tons/year

3. Coke

   Physical Properties (Perry, 1997):
   - Formula : C
   - Formula weight, g/mol : 12.01
   - Specific gravity : 0.37-0.51
   - Melting point at 1 atm, °C : >3500
   - Boiling point at 1 atm, °C : 4200
   - Formation heat, kcal/mol : 0
   - Gibbs energy, kcal/mol : 0

   Chemical properties (Kirk and Othmer, 1981):
   - React with oxygen and vapor
   - Not corrosive

b) Products

1. Titanium Dioxide

   Physical Properties (Perry, 1997):
   - Formula : TiO₂
   - Formula weight, g/mol : 79.90
   - Melting point at 1 atm, °C : 1855
   - Boiling point at 1 atm, °C : 2500-3000
   - Formation heat, kcal/mol : -225
   - Gibbs energy, kcal/mol : -211.9

   Chemical properties (Kirk and Othmer, 1981):
   - Not easy to explode
   - Insoluble in water
   - Not corrosive
2. Iron (III) Chloride

Physical Properties (Perry, 1997):
- Formula: FeCl₃
- Formula weight, g/mol: 162.22
- Specific gravity: 2.804
- Melting point at 1 atm, °C: 282
- Boiling point at 1 atm, °C: 315
- Formation heat (l), kcal/mol: -128.5
- Formation heat (g), kcal/mol: -129.5
- Gibbs energy (l), kcal/mol: -96.5
- Gibbs energy (g), kcal/mol: -97.8

Chemical properties (Kirk and Othmer, 1981):
- Corrosive
- Insoluble in water

1.4.4. Process Description

Titanium dioxide is produced from the reaction between titanium dioxide ore contained in ilmenite with chlorine gas in the fluidized bed reactor at a temperature of about 900°C at atmospheric pressure with the addition of coke as a reducing agent. The reaction occurs as follows:

1. Coke Combustion Reaction (Hughes, 1971)
   \[ \text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \quad (1-2) \]

2. Ilmenite Chlorination Reaction (Li-ping, 2013)
   \[ \text{TiO}_2 + 2\text{Cl}_2 + 2\text{CO} \rightarrow \text{TiCl}_4 + 2\text{CO}_2 \quad (1-3) \]
   \[ \text{Fe}_2\text{O}_3 + 3\text{Cl}_2 + 3\text{CO} \rightarrow 2\text{FeCl}_3 + 3\text{CO}_2 \quad (1-4) \]

FeCl₃ formed from Fe₂O₃ contained in ilmenite. Chloride non-volatile, residual coke and unreacted impurity ore ilmenite are removed from the gas stream through the bottom chlorinator. Out of chlorinator, the product temperature reaches 900°C. The stream of products in the form of gas is purified to separate the TiCl₄ from other gases through condensation, so that
the product is entered into the cooler and cooled until the temperature reaches 170°C which FeCl₃ be condensed and then do the cooling again until the temperature reaches 40°C, and TiCl₄ already condensed. Flue gases such as CO, CO₂, N₂, and Cl₂ are supplied to the absorber for separation Cl₂ gas using caustic solution. Then the top products of the absorber will be channeled to the stack, where the CO is converted to CO₂, which would then be discharged into the atmosphere. Pure TiCl₄ condensed incorporated into the oxidation reactor. Pure TiCl₄ is vaporized and oxidized in the oxidation reactor at a temperature of 1000°C uses oxygen from the air to form titanium dioxide and chlorine gas. The reaction occurs as follows:

\[
\text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2
\]  

Stream containing chlorine gas and TiCl₄ is recycled toward chlorinator output. Pure TiO₂ solids passed to the final stage, namely cooling and packaging to be marketed.