Optimization Process In The Synthesis of Stannous Chloride (SnCl₂) by Redox Method In The Context of Downstream Tin Derivative Product

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Abstract. Indonesia has been known as the Tin Island in Southeast Asian Tin Belt region. This makes Indonesia listed as the second biggest tin producer in the world after China, with production reached 33.444 metric tons. However, 95% of tin which has been exported is still in the form of bars, not the optimal downstream tin derivative products, especially in the form of tin chemicals such as SnCl₂. It turned out that tin chemical products are imported to meet the needs of domestic industry. In 2014, tin import reached USD 200 million. As one of the downstream products of tin derivatives, SnCl₂ can be used as a catalyst, reducing agent, and as the main ingredient for other tin derivative products. This research was conducted based on the demand of industry, PT Timah Industrid, to study the synthesis of SnCl₂ powder in optimum conditions with redox method. The tin powder was dissolved in concentrated HCl heated on a hotplate, with variations in the particle size of the tin, HCl concentration and the reaction temperature. Differential Thermal Analysis (DTA) was carried out at 800°C with a heating rate of 10°C/min⁻¹. The morphological structure of SnCl₂ powder can be determined using 3D-Optical Microscope VHX-5000. As for the SnCl₂ phase, it can be identified using the Rigaku SmartLab X-ray diffraction. This attempt has succeeded in synthesizing SnCl₂ powder at optimum conditions with a yield percentage of 95%.

1. Introduction
Large deposit of tin metal (Stannum/Sn) in Indonesia makes this country dubbed as the second largest tin producer in the world after China [11]. Through mining company PT Timah, in 2018, Indonesia has been able to produce tin by 33.444 metric tons with a percentage rise of 10.6% [3]. Until now, tin ore resources in Indonesia have reached 1.043.633 tons while the tin ore reserves reached 415.359 tons [9]. Tin is one of Indonesia’s main export commodities. However, 95% of Indonesia’s tin metal commodities are used to meet the needs of foreign markets and only around 5% is used to meet the domestic market [10]. The exported tin commodity is still in the form of bars whereas government regulations have emphasized that there must be an increase in added value in local strategic mineral
ore processing [7] by increasing the processing industry that provides high added value and reducing the export of raw materials [5]. The government also regulates that exported tin must have a Sn content of 95% so that each process will produce by-products and tin scrap outside the specifications of industry needs. It is essential to improve tin by products and scrap downstream in order to increase its value and automatically applies the principle of zero waste in the industry. On the other hand, domestic and international industries require downstream tin products in the form of tin chemicals. Therefore, this research will focus on downstream tin derivative products in the form of tin chemicals especially Stannous Chloride (SnCl2). Stannous Chloride is industrially important tin chemicals. Stannous Chloride is used in surface treatment, as a catalyst, as a reducing agent, and as other tin derivative raw material [2]. There are several methods for synthesizing SnCl2 namely by reacting Sn and HCl to produce SnCl4 in solution [1]. Synthesis of SnCl2 can be done by recalculating lead powder into 32% HCl and sonication at 800W 24 kHz [12]. SnCl2 is produced by reacting 60% SnCl4 and lead granules [2]. However, this method needs to be reconfirmed if it is to be applied in real industries. Thus, it is necessary to conduct more detailed, simple and easy applicable research in the real industry. This research was carried out based on the industry of PT Timah Industrici which focused on the development of tin chemicals, namely SnCl2. This study aims to study and determine the optimum conditions in producing laboratory scale SnCl2 powder. Furthermore, it will be developed on a micro scale which will then be scaled up to industrial scale.

2. Experiment

Powdered (p-Sn), granulated (g-Sn), flakes (f-Sn) and 37 wt% hydrochloric acid (HCl) are employed in this research. The results of the tin atomization process that did not meet the industry requirements specifications were used as a source of tin. There are several variations in the size of tin particles. Then, the sifting was carried out to produce 500 mesh, 400 mesh and 200 mesh p-Sn particle sizes. HCl concentrations were used in the 6-12 M. The synthesis of SnCl2 was started by dissolving p-sn into HCl by chemical reaction as follows:

\[ \text{Sn (s)} + 2\text{HCl(l)} \rightarrow \text{SnCl}_2(\ell) + 2\text{H}_2(\text{g}) \]  \quad (1)

\[ \text{SnCl}_2(\ell) + \text{heating} \rightarrow \text{SnCl}_2(\text{cr}) \]  \quad (2)

SnCl2 was prepared by reacting p-Sn 2.5 g 500 mesh with 37% HCl at 80°C above the hotplate in the water bath then stirred at a speed of 200 rpm in open state. The reaction that has taken place produced a concentrated clear solution (SnCl2 solution) and white precipitate slowly formed. After 120 minutes, the stirrer was turned off and the sample remained heated on the hotplate until SnCl2 crystals were obtained. The sample was cooled at room temperature then calcined using a furnace at 200°C with a heating rate of 10°C min⁻¹ for 60 minutes. Then, it was cooled at room temperature and crushed with mortar to produce SnCl2 powder. The steps were repeated for tin particle sizes of 400 mesh, 200 mesh, granules and flakes.

To investigated the effect of acid concentration, SnCl2 was prepared by reacting p-Sn 2.5 g 500 mesh with HCl 11 M at 80°C above the hotplate in the water bath then stirred at 200 rpm. The reaction that has taken place produce a concentrated clear solution (SnCl2 solution) and white precipitate slowly formed. After 120 minutes, the stirrer was turned off while still heating the sample on a hotplate until SnCl2 crystals were obtained. After that, the sample was cooled at room temperature. The steps were repeated at 10 M, 9 M and 6 M HCl concentrations.

Similarly, to investigate the effect of reaction temperature, SnCl2 was prepared by reacting p-Sn 2.5 g 500 mesh with HCl 12 M at 90°C above the hotplate in the water bath then stirred at 200 rpm. The reaction that has taken place produce a concentrated clear solution (SnCl2 solution) and white precipitate slowly formed. After 120 minutes, the stirrer was turned off while still heating the sample on a hotplate until SnCl2 crystals were obtained. The sample was then cooled at room temperature. The steps were repeated at 70°C dan 60°C.

Samples were then characterized using Differential Thermal Analysis at room temperature up to 800°C with a heating rate of 10°C min⁻¹. The morphological structure of the sample can be seen using
3D Optical Microscope vhx-5000. Meanwhile, to determine the XRD pattern, the samples were characterized using The Rigaku SmartLab X-ray diffraction

3. Results and Discussion

Tin from the atomization process that did not meet the industry requirements specification were used as a source of p-Sn in this research. Meanwhile, the source of Cl\(^-\) ions were taken from 37 wt%HCl, because HCl is the best source of Cl\(^-\) ions compared to the others [1] [8]. The chemical reaction are as follows:

\[
\text{Sn} \,(s) + 2\text{HCl} \,(l) \rightarrow \text{SnCl}_2 \,(l) + 2\text{H}_2 \,(g) \quad (3)
\]

\[
\text{SnCl}_2 \,(l) + \text{heating} \rightarrow \text{SnCl}_2 \,(cr) \quad (4)
\]

There are three variables evaluated in this study namely p-Sn particle size, HCl concentration and reaction temperature. The purpose of the three treatments were to find out the optimum results and conditions in the synthesis of SnCl\(_2\) where these three would influence each other. The first treatment of the effect of p-sn particle size with the resulting SnCl\(_2\) yield can be seen in Figure 1, below:

![Figure 1](image1.png)

**Figure 1.** The relationship of Sn Particle Size with Yield of SnCl\(_2\)

The sample conditions were reacted at 80\(^\circ\)C with a concentration of 12 M HCl and the reaction was open. Based on the graph above the finer the Sn particle size, the easier it is to react, the greater yield is. In this research, the optimum Sn particle size was 500 mesh.

The second treatment of the effect of the reaction temperature with the resulting sncl2 yield can be seen in figure 2 below:

![Figure 2](image2.png)

**Figure 2.** The relationship between HCl concentration and SnCl\(_2\) yield.
The particle size of Sn was 500 mesh, the reaction temperature was $80^\circ C$ with the reaction took place in open state. Figure 2 shows that the concentration of HCl is directly proportional to the SnCl$_2$ produced which will tend to produce more and more products. In this research, the most optimum concentration of HCl was 12 M. The third treatment effect of the reaction temperature with the resulting SnCl$_2$ yield can be seen in figure 3 below.

![Graph showing the relationship between HCl concentration and SnCl$_2$ yield.](image)

**Figure 3.** The relationship between HCl concentration and SnCl$_2$ yield.

The sample conditions were Sn 500 mesh, particle size 12 M HCl concentration, and the reaction was open. Figure 3 shows that increasing the temperature tend to increase the speed of reaction, and therefore produce higher yield. However, further increasing the temperature to $90^\circ C$ decreases the yield significantly. In this research, the most optimal temperature occurred when the reaction took place at $80^\circ C$ and the temperature tone of $90^\circ C$ has decreased yields. It is possible because the reaction took place in an open state while the nature of HCl is relatively volatile. In high temperatures especially, HCl evaporates more quickly into the environment and the vapor does not react with Sn particles so that the resulting final product will also be reduced.

![Graph showing DTA analysis.](image)

**Figure 4.** The results of the SnCl$_2$ sample analysis use Differential Thermal Analysis. (a) Commercial SnCl$_2$, (b) SnCl$_2$ T $80^\circ C$, (c) SnCl$_2$ T $200^\circ C$, (d) SnCl$_2$ T $200^\circ C$ holding 60 min, (e) SnCl$_2$ T $400^\circ C$. 
To evaluate the purity of the SnCl₂ product, the as-synthesized SnCl₂ was placed in crucible 1 and A second powder was placed in crucible 2. The heating was started from room temperature to 800°C with a speed of 10°C min⁻¹. After cooling down to room temperature, a white powder was found at the bottom of the crucible. For comparison, commercial SnCl₂ powder was analyzed using DTA with the results of endothermic and an exothermic peak. In the SnCl₂ samples at 80°C reaction temperature, the as-synthesized SnCl₂ show three endothermic peaks and an exothermic peak. After the SnCl₂ sample was heated at 200°C, two endothermic peaks remained but they were not really clear. Meanwhile, one endothermic followed by one exothermic peak remained. Then the SnCl₂ sample was reheated at 200°C with a holding time of 60 minutes. The DTA result reveals an endothermic and an exothermic peak. This result is in accordance with the DTA curve in commercial SnCl₂. To ensure were would be other peaks, the samples were heated again in 400°C where it turned out that all the peaks disappeared. This means that the SnCl₂ phase will be formed under optimum conditions at a temperature of 80°C and furnace heating at 200°C for at least 60 minutes. The lack of peak clearly indicates the absence of the oxidation of molten SnCl₂ at higher heating rates [4] as shown in figure 4 point (e).

**Figure 5.** The results of SnCl₂ morphology using 3D Optical Microscope vhx 5000.

(a) SnCl₂ Commercial and pictures (b) SnCl₂ Synthesis. Both have an average particle size above 100 um. In this study the synthesized sample has a smaller SnCl₂ particle size than commercial SnCl₂. But experiencing agglomeration. This difference is possible for the existence of different methods for synthesizing SnCl₂.

The results of characterization using XRD on the synthesized SnCl₂ have the same XRD pattern with commercial SnCl₂. Again, this result corroborates the characterization result by DTA which indicates that the SnCl₂ obtained is of excellent purity.
Figure 6. The results of SnCl$_2$ sample analysis using x-ray diffraction. (a) commercial SnCl$_2$ samples, (b) SnCl$_2$ T 80$^\circ$C, (c) SnCl$_2$ T 200$^\circ$C, (d) SnCl$_2$ T 200$^\circ$C holding 60 min.
4. Conclusion
The synthesis of Stannous Chloride (SnCl₂) was successfully carried out. Based on the result of the research, the optimum conditions are as follows. The finer the particle size of tin, the higher concentration of HCl, and the higher the reaction temperature, the higher the final product will be. Based on the results of the research, the optimal efficient condition is when the tin powder particle size is 500 mesh with HCl 12 M at 80°C with a percentage of 95%.

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