Waste Management In Petroleum Refinery Spent Catalyst

by

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Dissertation submitted in partial fulfillment of
the requirements for the
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SHAFIQ BIN SULAIMAN

ABSTRACT

Solid catalysts containing metals, metal oxides or sulfides supported on an alumina carrier, which play a key role in the refining of petroleum to clean fuels and many other valuable products, become solid wastes after use. In many refineries, the spent catalysts discarded from hydro processing units form a major part of these solid wastes. Disposal of spent hydro processing catalysts requires compliance with stringent environmental regulations because of their hazardous nature and toxic chemicals content. Various options such as minimizing spent catalyst waste generation by regeneration and reuse, metals recovery, utilization to produce useful materials and treatment for safe disposal, could be considered to deal with the spent catalyst environmental problem.

In the present work, attention was focused on the recovery of alumina as aluminium trihydroxide from spent Ni/Al_2O_3 catalyst. More than 93% recovery of alumina in the form of aluminium trihydroxide was achieved using the dry roasting method. Alumina reacted with NaOH forming sodium aluminate from which aluminium trihydroxide was precipitated. The effect of temperature with constant 1:3 mole ratio to the amount of aluminium trihydroxide recovered was studied.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Catalytic processes are integral to the petroleum refining and petrochemical industries, and large amounts of catalysts are used in numerous processes in these industries [1]. The catalysts have regulated life and they deactivate with time during use in a process [2]. The deactivated catalysts are usually regenerated and reused. However, when it is uneconomical to regenerate and reuse them, they are discarded as spent catalysts. Usually, most of these catalysts would include metals in the form of oxides or sulfides either supported on or mixed with a carrier such as alumina. For, example, the spent catalyst, discarded from the hydro processing units contain sulfides of V, Mo, Ni and Co and Al_2O_3, and that dismissed from the steam reforming and methanation units contain NiO and alumina. As these spent catalysts are hazardous wastes, their disposal in landfills is restricted. In recent years, rising emphasis has been placed on the progress of processes for recycling the waste catalyst materials as much as possible. Several achievable routes such as metals recovery, rejuvenation and reuse; treatment to produce active new catalysts and other useful materials have been studied by refiners to handle the spent catalyst problem [3].

1.2 Problem Statement

Recovery of metals and other valuable products from spent catalysts is a smart option. Recovery metals such as V, Mo, Ni and Co from spent hydro processing catalysts have been described in many studies. Several processes such as chlorination [4], acid leaching [5], alkali leaching [6], two stage leaching with acid and alkaline solutions, roasting with sodium salts [7], treatment with ammonia and ammonium salt solutions [8], bioleaching and electrochemical dissolution have been conveyed in the literature for recovery of metals from spent hydro processing catalysts. Extraction of nickel from nickel-containing waste catalysts has also been reviewed by many researchers [9]. Knowledge on the recovery of the alumina, which forms a main part of the spent catalyst, is absent in most of these studies, although in some studies, alumina has been reclaimed as aluminium salts or as fused alumina. Preparation of α-alumina from an alumina-containing spent hydro treating catalyst was reported in recent study [8]. Recovery of alumina as boehmite, which is an important precursor for γ-alumina and many other special grades of aluminium oxides, appears to have received little attention in the prior studies.

1.3 Objective and Scope of Study

The objective of the project is to classify and develop a lab scale process to reclaim alumina as aluminium trihydroxide [$Al(OH)3$] from an alumina-supported spent catalyst.

The scope of work in this project will only look at a specific type of catalyst, which is an alumina-based catalyst. The author would study the effect of temperature on the extend of recovery of from aluminium trihydroxide [$Al(OH)3$] spent catalyst by dry roasting with NaOH. The design of experiment would be an adaptation from an available process.

CHAPTER 2
LITERATURE REVIEW

2.1 Spent Catalyst Waste Management

In the petroleum refinery processes, solid catalysts arc widely used to improve the process efficiency. The catalyst materials typically contain chemicals (e.g. metals, metal oxide, metal sulfides, etc.), which simplify difficult hydrocarbons transformations with high selectivity and authorize the refiners to produce the full range of clean transportation fuels with desired specifications from petroleum distillates and residues. Thus, for instance, production of clean diesel fuels with low-sulfur levels is attained by hydro treating sulfur-containing gas–oil streams in the existence of catalysts comprising Mo and Co or Mo and Ni on $Al2O3$. Catalysts are also greatly used in the conversion of heavy oils and residues to more valuable light and middle distillates and feedstock for petrochemicals [10]. The marvelous flexibility of the catalytic chemistry permits the refiners to respond quickly to changes in market needs and product specifications as well as to the alterations in feedstock quality.

The catalysts used in the refining processes deactivate with time [11]. When the activity of the catalyst falloff below the satisfactory level, it is typically regenerated and reused, but regeneration is not always achievable. After a small number of cycles of regeneration and reuse, the catalyst activity may fall to very low levels and additional regeneration may not be economically feasible. The spent catalysts are redundant as solid wastes.

The amount of spent catalysts dismissed from different processing units depends essentially on the amount of fresh catalysts used, their life and the quantity of deposits formed on them during usage in the reactors. In majority of refineries, a main portion of the spent catalyst wastes originated from the hydro processing units because of the use of enormous quantities of catalysts in the hydro treating processes for the purification and improvement of various petroleum streams and residues.

The capacity of spent hydro processing catalysts discarded as solid waste has amplified significantly in recent years due to the following reasons:

(i) A prompt growth in the distillates hydro treating capacity to meet the rising demand for ultra-low sulfur transportation fuels.
(ii) Reduced cycle times due to higher severity operations in diesel hydro treating units.
(iii) A stable increase in the processing of heavier feedstock comprising higher sulfur and metal contents to distillates by hydrogen addition technology.
(iv) Rapid deactivation and unavailability of reactivation process for residue hydro processing catalysts.

The market demand for hydro treatment catalysts is valued to increase with a yearly growth rate of 4.4% [3]. Presently, the market for fresh hydro treatment catalyst is around 120,000 t/year, 50% of which is used for hydro treatment of distillates to make clean fuels and the other 50% is used for residue upgrading and purification [4]. The hydrocracking catalyst market, which is approximately around 10,000t/year, is also expected to grow at a rate of about 5% per year [4]. The sum of spent catalysts rejected from the hydro treating units is constantly higher than that of the fresh catalyst amount loaded in the reactor because of the configuration of coke, sulfur and metal deposits on the catalysts during the hydro treating process. For instance, spent catalysts from distillate hydro treating units comprise normally 10–20% carbon and 7–15% sulfur together with some oil. In the event of residue hydro processing operations, metals such as V and Ni present in the feed deposit on the catalyst together with coke. The spent catalysts rejected from these units typically contain 7–20% V+Ni, 15–25% coke, 7–15% sulfur and 5–10% residual oil together with active metals (Mo and Co or Ni) and Al_2O_3 originally exist in the catalyst. The sum quantity of spent hydro treating catalysts generated worldwide is in the range of 150,000–170,000 t/year [4].

Discarding of spent catalysts compels compliance with stringent environmental guidelines. Spent hydro processing catalysts have been categorized as hazardous wastes by the environmental protection agency (EPA) in the USA. The EPA added spent hydro treating catalyst (K171) and spent hydro refining catalyst (K172) to its hazardous waste list in August 1998 because of their self-heating behavior and toxic chemicals content [3]. Spent hydrocracking catalyst was added to the list in 1999. Metals such as Co, Ni and V that exist in spent hydro processing catalysts are contained in the list of potentially hazardous wastes published by the Environment Canada. These metals can be leached by water after disposal and pollute the environment. Besides the formation of leachates, the spent hydro processing catalysts can liberate toxic gases when interact with water. The foundation of the dangerous HCN gas from the coke deposited on hydro processing catalysts that comprises a substantial quantity of nitrogen has been reported. Spent catalysts come under the controlling terms of the Basel Convention and Organization for Economic Cooperation and Development (OECD) rules and cannot be exported to third world countries. Furthermore, the producing works or "generators" of the catalyst have a legal obligation to guarantee that their spent catalysts are correctly disposed of or securely recycled. The USA pioneered the principle that waste remains forever the generator's responsibility and this is being accepted throughout the rest of the developed world.

2.2 **Reclamation of Alumina as Boehmite**

Boehmite is an important precursor material for $\gamma\text{-}Al_2O_3$, which is widely used as a support in many industrially important catalysts. Boehmite is usually prepared by precipitation from solutions of aluminum salts and sodium aluminate under hydrothermal conditions. For example, boehmite was prepared with a variety of crystallite sizes from solutions of aluminum nitrate and sodium aluminate. Boehmite was also acquired from aqueous solutions of aluminum chloride and sodium hydroxide. Urea has been used as a reagent for precipitating boehmite hydrothermally from aqueous solutions of different aluminum salts such as $Al(NO_3)_3$, $Al_2(SO_4)_3$ and $AlCl_3$.

The waste alumina material present in spent catalyst would be converted first to bayerite and then to boehmite by hydrothermal treatment. Conversion of bayerite to boehmite under hydrothermal conditions essentially involves removal of 1 mol of H_2O per mole of bayerite by dehydration.

Hanadi Al-Sheeha, Meena Marafi, Antony Stanislaus [12] studied the reclamation of alumina through several methods:

1. Dry roasting method

   In this method, the effect of temperature and the influence of changing mole ratio between Al_2O_3 and NaOH on the extent of recovery of Al_2O_3 from spent catalyst by dry roasting with NaOH.

2. Wet digestion method

   In this method, the spent catalyst was mixed with NaOH solution of required concentration and this mixture was stirred in a high pressure autoclave at different temperatures in the range 150–250 °.

3. Preparation of boehmite and γ-Al_2O_3 from $Al(OH)_3$

   To prepare the final end product, the aluminium trihydroxide [$Al(OH)_3$] obtained from the spent catalyst by digestion with NaOH followed by precipitation with CO_2 was subjected to hydrothermal treatment in a high pressure autoclave at a temperature of 180 °C for 16 hours.

2.3 Methods for Experiment

The spent catalyst extrudes will be crush in a grinding and sieved to obtain spent catalyst powder with particle size less than 106 µm. The spent catalyst powder will be calcine in air at 550 °C and cooled to room temperature prior to metal recovery experiments.

Alumina will first dissolve as sodium aluminate from the spent catalyst by treatment with NaOH leaving NiO as an insoluble residue. Two methods namely, wet digestion and dry roasting will be use for treatment of the spent catalyst with NaOH.

In the wet method, spent catalyst powder will be mix with NaOH solution and the mixture will be heated in an autoclave, at the desired temperature with continuous stirring for three hours. Alumina present in the spent catalyst will react with NaOH and would be converted to sodium aluminate under these conditions. The autoclave will then cool down and the solution will be filtered. The residue would contain NiO and the solution will contain sodium aluminate. $Al(OH)_3$will be precipitated from the sodium aluminate solution by passing CO_2.

In the dry roasting method, the spent catalyst powder will be mix with powdered NaOH in different ratios (1:2 to 1:4) and would be roasted in a muffle furnace at different temperatures in the range 400–700 °C for 2 hours in order to study the effect of temperature on aluminium and nickel recovery. When the spent catalyst containing NiO and Al_2O_3 is heated with NaOH at high temperatures, Al_2O_3 reacts with NaOH forming sodium aluminate. The nickel oxide present in the catalyst does not react with NaOH. The roasted product will then be extracted with distilled water at 100 °C for 1 hour to dissolve the sodium aluminate. The solution will than filtered to separate the sodium aluminate from the unreacted NiO residue.

The $Al(OH)_3$ obtained in the above two methods would be in bayerite form. It will be converted to boehmite by hydrothermal treatment a high-pressure autoclave. In a typical experiment 40 g of dried $Al(OH)_3$ would be mixed with 200 ml of water and heated in the autoclave at 180 °C for 18 hours with continuous stirring. During the hydrothermal treatment, $Al(OH)_3$would be converted to boehmite [AlO(OH)]. The boehmite formed in the process would be filtered, dried and characterized by X-ray diffraction (XRD). The boehmite would then change to γ-Al_2O_3 by calcination at 500 °C for 4 hours.

Figure 2.1 below shows the flow scheme for recovery of alumina as boehmite from spent Ni/Al_2O_3 catalyst:

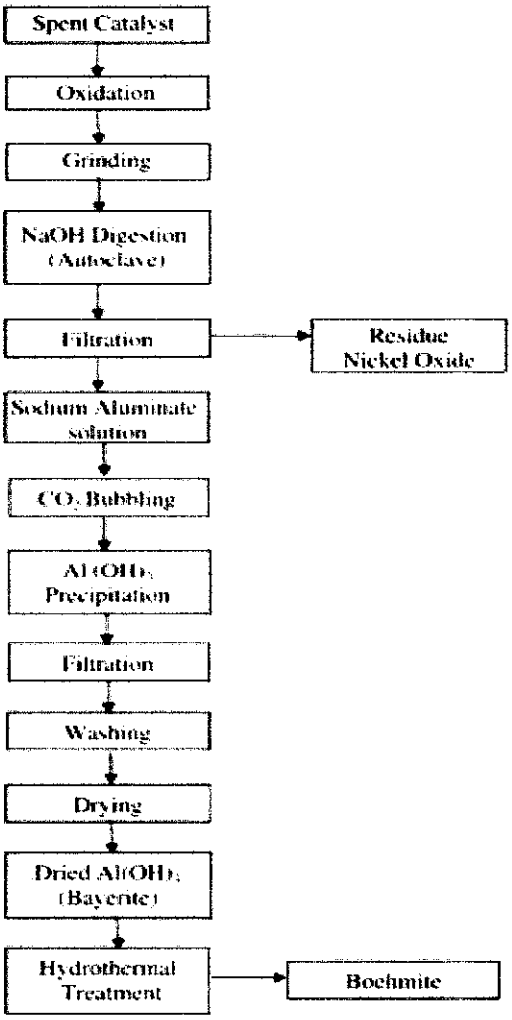

Figure 2.1 Flow scheme for recovery of alumina as boehmite from spent catalyst [12].

CHAPTER 3

METHODOLOGY

3.1 Flow Chart

Figure 3.1 below shows the basic steps of this project:

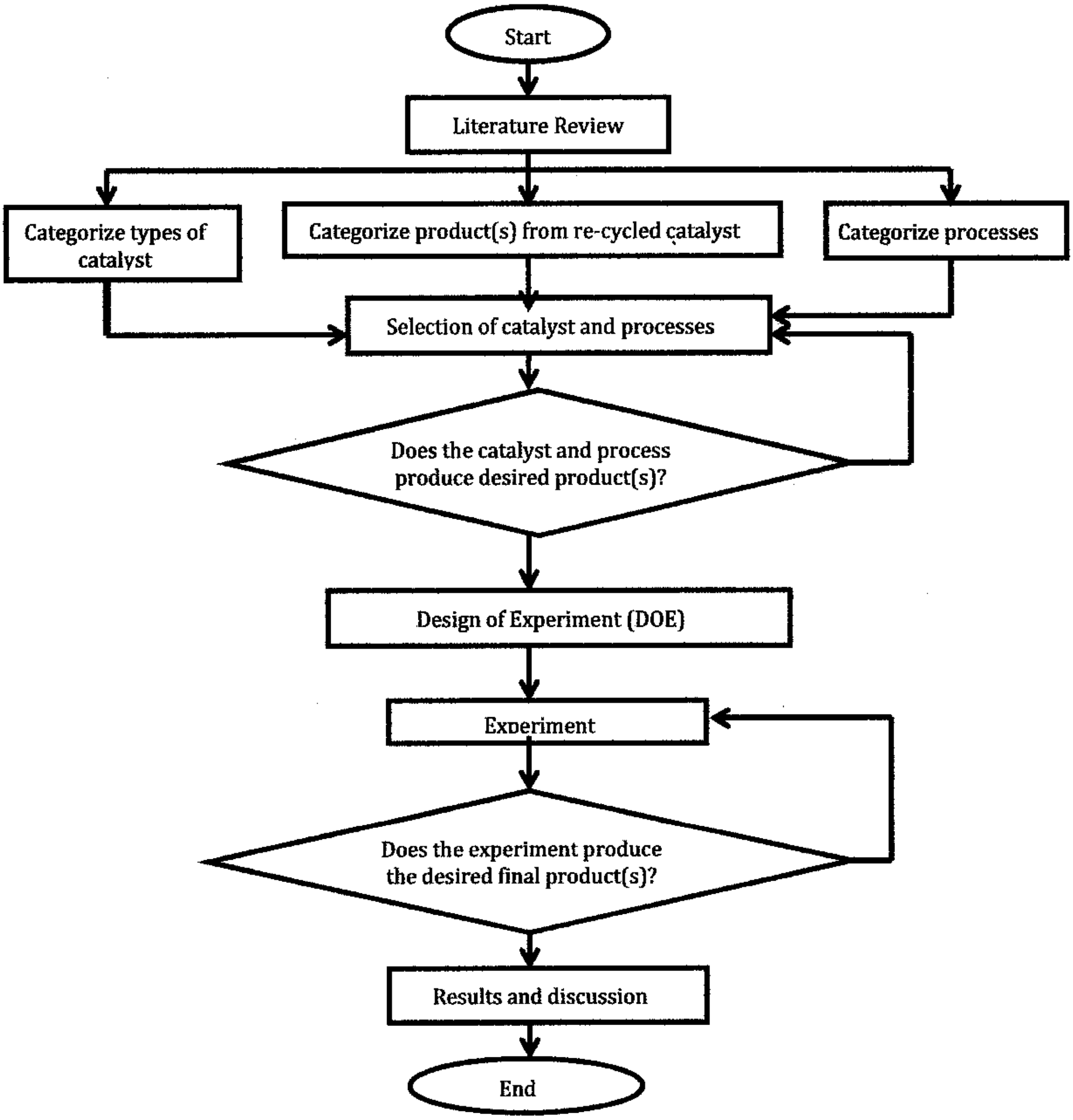

Figure 3.1 Methodology of the project

3.2 Gantt Chart

Table 3.1 below shows the planning and flow of the project:

Table 3.1 Gantt chart for project

No	Week/ Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Literature review	■	■	■											
2	Selection of catalyst and processes • Categorize types of catalyst • Categorize products from re-cycled catalyst • Categorize processes		■	■	■	■	■	■							
3	Experiment work							■	■	■	■	■	■	■	
4	Results and discussion													■	■

3.3 Identifying types of catalyst, processes and end product

Table 3.2 below shows the types of catalyst, its processes and the end product.

Table 3.2 Type of catalysts, processes and end product(s)

No	Catalyst(s)	Processes	End product(s)
1	Vanadium-rich spent refinery catalyst	Chemo-lithorophic sulfur oxidizing catalyst (bioleaching)	Nickel, Molybdenum, Vanadium
2	Spent catalyst saturated with zinc acetate	Effect of microwave penetration on zinc extraction	Zinc
3	Spent sulfuric acid catalyst	Alkaline and acidic leaching	Vanadium, Nickel
4	Alumina supported spent catalyst	Treatment with caustic soda	Recovery of alumina as aluminium trihydroxide
5	Spent vanadium catalyst	Leaching in urea solution	Vanadium, Potassium, Iron
6	Spent zeolite catalyst	Reuse of spent catalyst in cement mortar	Fine aggregate in cement mortar

From table 3.2, the chosen spent catalyst to be studied is the alumina supported spent catalyst which would produce alumina as aluminium trihydroxide [$Al(OH)_3$].

3.4 Catalyst

The author had acquired spent alumina based catalyst from DIALOG Catalyst Services Sdn Bhd (DCSSB) in order to complete this study.

Figure 3.2 Catalyst acquired from DIALOG Catalyst Services Sdn. Bhd.

Properties of the catalyst are shown in the table 4.1 below:

Table 4.1 Properties of spent catalyst (alumina-based)

Ingredient & Cas No	% Weight	Acgih Tlv-Twa	Osha Pel-Twa	Units
Aluminium oxide (non fibrous) 1344-28-1	<95	10	15(TD) 5(R)	Mg/m3
Water 7732-18-5	<15	N.E	N.E	N.A
Sodium Oxide 1313-59-3	<10	N.E	N.E	N.A

Source: DIALOG Catalyst Services Sdn Bhd.

Abbreviations:

N.A – Not applicable
N.E – None established
SC – Soluble Compounds
IS- Insoluble
RD – Respirable dust
TD – Total dust
FuD – Fume and dust
Fu- Fume
I - Inhalable
R – Respirable

3.5 Experimental Work

The experiment was conducted at Block 17, Mechanical Engineering block in Universiti Teknologi Petronas (UTP). Prior conducting the experiment, the author carefully studied the material safety data sheet (MSDS) and UTP lab rules was observed in order to prevent any injuries. Due to limited time, the author only managed to reclaim alumina using the dry roasting method.

The experiment was conducted as follow:

1. The spent catalyst was crushed using the Mortar grinder for four (4) minutes.

Figure 3.3 Alumina-based catalysts acquired from DIALOG Catalyst Services Sdn Bhd

Figure 3.4 Alumina-based catalysts in mortar grinder's container

Figure 3.5 Mortar grinder used in the experiment

2. The crushed spent catalyst would be sieved to obtain spent catalyst powder with particle size less than 106 μm.

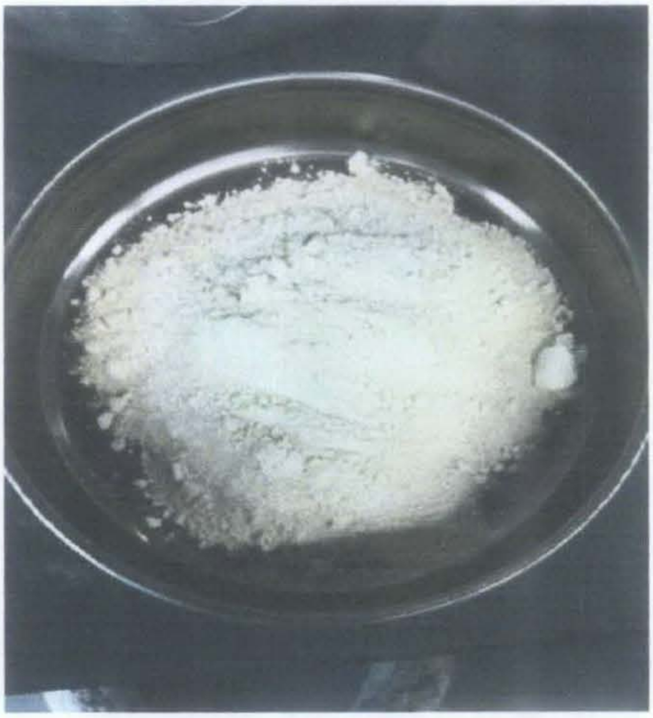

Figure 3.6 Crushed spent catalyst in sieving container

Figure 3.7 Sieving machine used in the experiment

3. The powdered spent catalyst was calcined in air at 550°C and cooled to room temperature

Figure 3.8 Carbolite furnace used in the experiment

4. 10g of powdered spent catalyst was mixed with 30g of powdered NaOH and heated up in the furnace at various temperatures. The temperatures chosen for this experiment was 425,450, 475, 500, 550, 700, 800 and 900 °C.

Figure 3.9 NaOH's weight was scaled prior to heat up

Figure 3.10 Spent catalyst's weight was scaled prior to heat up

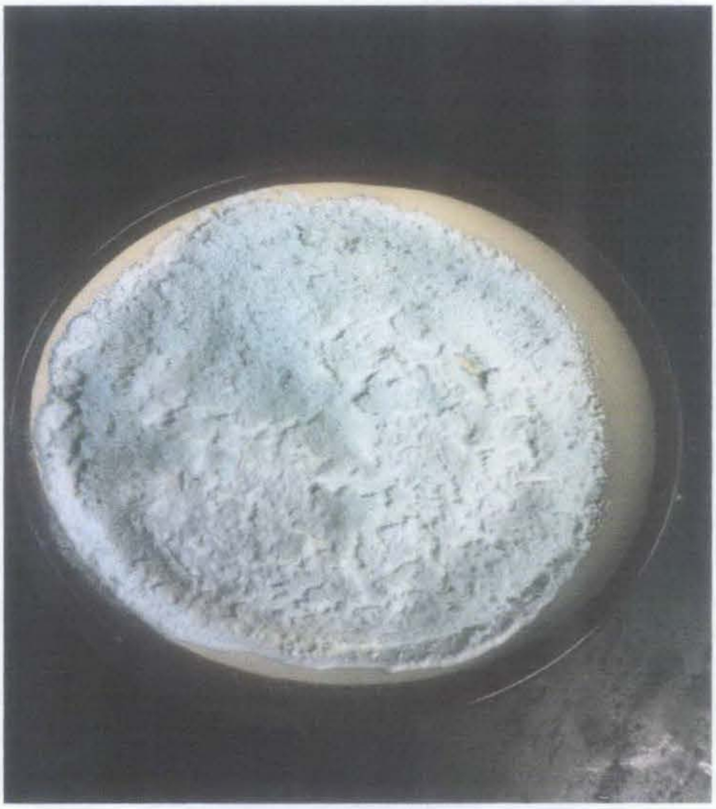

Figure 3.11 Roasted product (mixture of NaOH and spent catalyst)

5. The roasted product was then extracted with distilled water at 100°C for 1 hour.

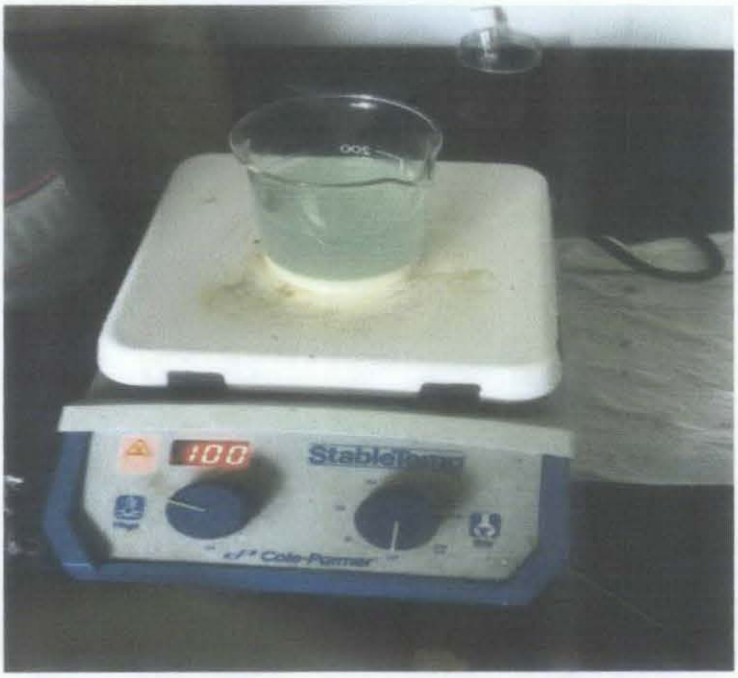

Figure 3.12 Roasted product diluted and heated up using hot plate

6. The solution was then filtered to separate the sodium aluminate from the NiO residue.

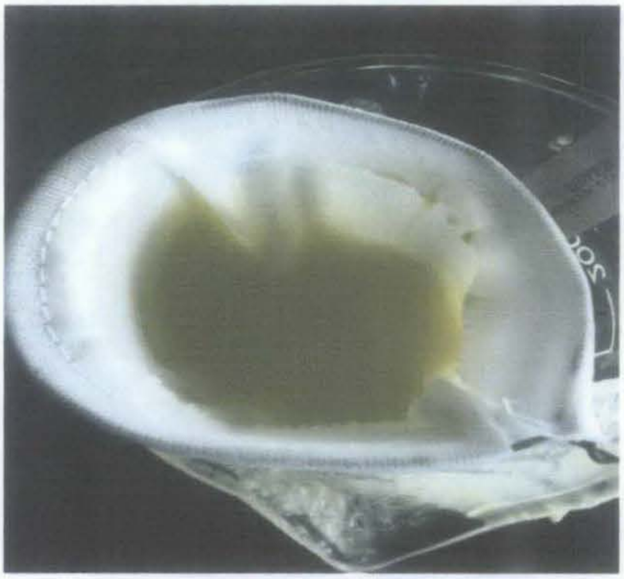

Figure 3.13 Solution filtered using filter

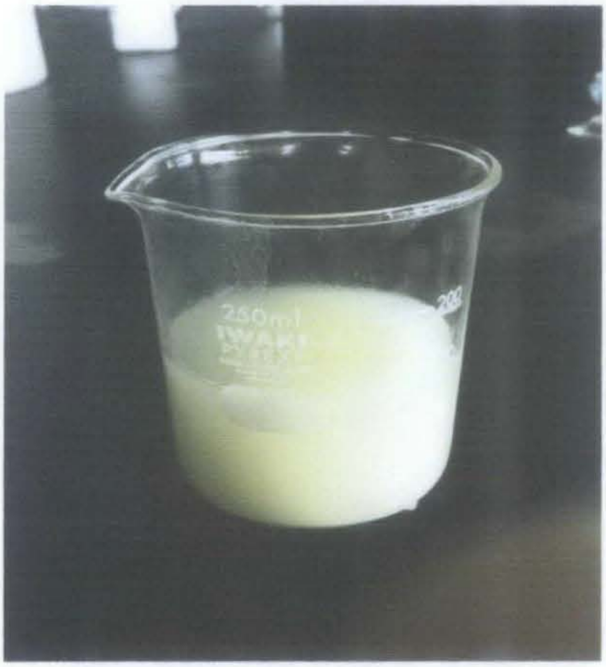

Figure 3.14 Solution of sodium aluminate

7. The filtrate sodium aluminate solution was neutralized by CO_2 bubbling for 2 hours.

Figure 3.15 Set up for CO_2 bubbling

Figure 3.16 Neutralized sodium aluminate from pH 13.5 to 7.3

8. The colloidal $Al(OH)_3$ formed by passing CO_2 filtered and washed with distilled water for several times.

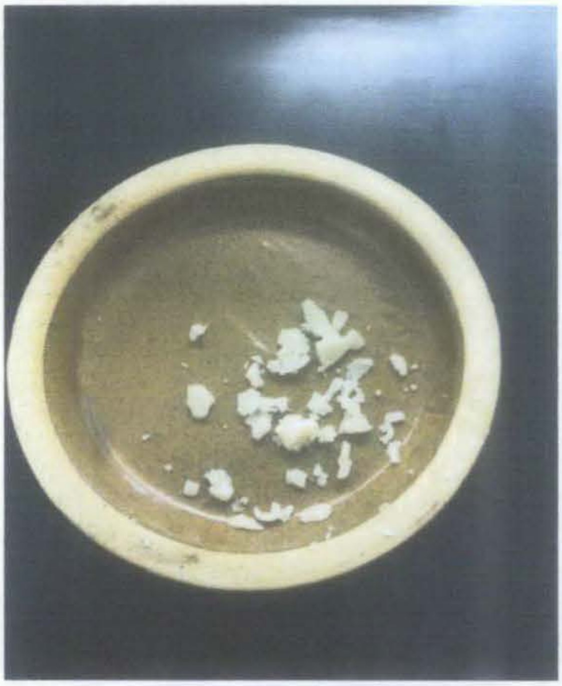

Figure 3.17 The colloidal $Al(OH)_3$ formed

9. The washed cake was dried at 110°C for 12 hours in order to get aluminium trihydroxide [$Al(OH)_3$].

Figure 3.18 Final product of aluminium trihydroxide [$Al(OH)_3$]

Figure 3.19 Closer look of final product of aluminium trihydroxide [$Al(OH)_3$]

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experiment Results

The results of the experiment conducted are tabulated in the table 4.2 below. A graph of percent alumina recovered versus temperature by dry roasting with NaOH was also presented in figure 4.1 to observe the effect better.

Table 4.2 Results of experiment

Temperature (°C)	Weight $Al(OH)_3$ (g)
425	25.8
450	26.7
475	27.6
500	28.2
550	24.6
700	21.9
800	15.0
900	9.6

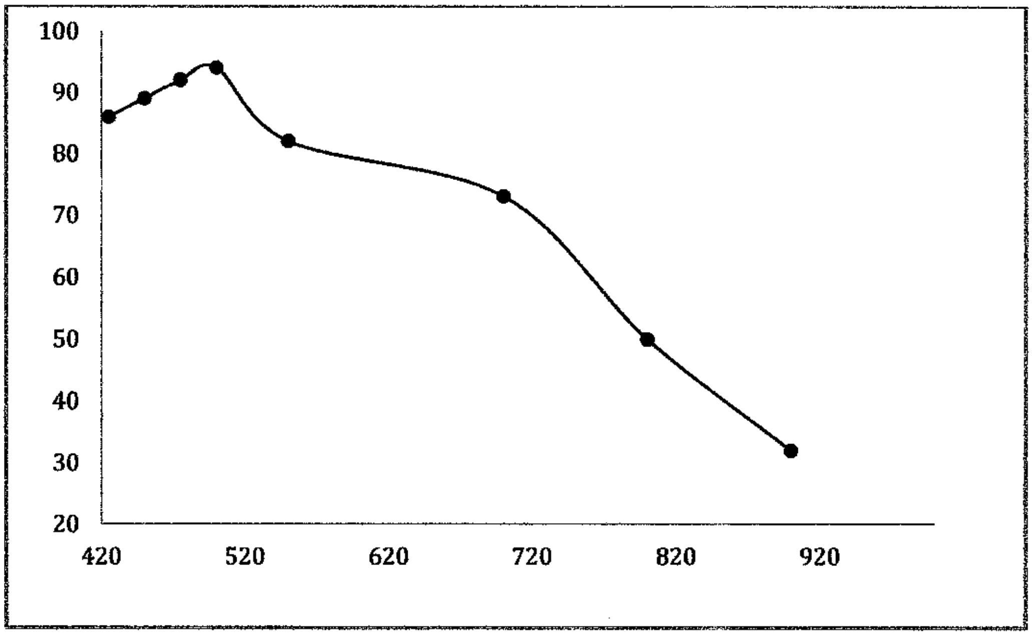

Figure 4.1 Graph percent alumina recovered versus temperature by dry roasting with NaOH

Table 4.2 and figure 4.1 illustrate the effect of temperature on the recovery of alumina in the form of aluminium trihydroxide [Al(OH)3], by roasting at a constant Al_2O_3 to NaOH mole ratio of 1:3 for 2 hours. It was observed that the alumina recovery increases outstandingly from 86% to 94% as the temperature is raised from 425°C to 500°C. An additional increase of the temperature above 500°C, leads to a strong decrease in alumina recovery.

Alumina recovery was reduced to 73%, 50% and 32% at the temperature of 700°C, 800°C and 900°C respectively. The reason for this low alumina recovery at high temperature is likely because at the mentioned temperature, Al_2O_3 sinters in the existence of NaOH and its surface area is reduced. Therefore, the contact between the NaOH and Al_2O_3 particles would be low which could result in lower reactivity between them.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Large quantities of spent catalysts containing valuable metals and alumina are discarded as solid wastes in the petroleum industries. Rising efforts have been dedicated in recent years in developing process for recycling the waste catalysts.

In the present work, emphasis was put on to recover alumina in the form of aluminium trihydroxide from an alumina-supported spent catalyst. The effect of temperature on the recovery of alumina was studied to achieve the objective of this study. From the experiment conducted, it is clear that temperature does play a significant role in the amount of alumina recovered. According to Table 4.2 and figure 4.1, the optimum temperature would be from 425°C to 500°C

Aluminium trihydroxide in the industry has many usages. They display exceptional flame retardant and smoke suppressant properties for thermoset and thermoplastics as well as elastomeric copolymers. They are intensely beneficial as fillers and coating pigments for fine printing papers for increased brightness, smoothness, and opacity. They are also useful as a reinforcing pigment in adhesives and adhesive tapes, and in waxes and polishes when a relatively soft and extremely fine mild abrasive is required.

5.2 RECOMMENDATION FOR FURTHER STUDIES

Further studies can be perform to extract alumina from the spent catalyst in a different type of forms such as boehmite and γ-$Al2O3$ which are considered as special grades that has many uses in the industry. Different approach can also be considered to reclaim this alumina such as the wet digestion method [12].

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