A PREPARATION OF NITRIC ACID FROM NITROGEN DIOXIDES USING PHOTOCATALYTIC METHOD

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JUDUL : **A PREPARATION OF NITRIC ACID FROM NITROGEN DIOXIDES USING PHOTOCATALYTIC METHOD**

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A PREPARATION OF NITRIC ACID FROM NITROGEN DIOXIDES USING PHOTOCATALYTIC METHOD

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A thesis submitted in fulfillment of the
requirement for the award of the Degree of
Bachelor in Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

DECLARATION

I declare that this thesis entitled "**A Preparation of Nitric Acid from Nitrogen Dioxides using Photocatalytic Method**" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....
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I owe this thesis and my true happiness I feel to my beloved parents,
Mr. Abdul Malek bin Jalil & Mrs. Rabiyah binti Fakir Mohd.
& my brothers, for their love and encouragement.

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ABSTRACT

A research is conducted to study on preparation of nitric acid from nitrogen dioxides using photocatalytic method. Due to the increasing pollution of oxides of nitrogen (NO_x), production of nitric acid is vital in reducing the oxides of nitrogen release to the atmosphere. Nitric acids are one of the most important inorganic acids and commonly used as laboratory reagent and an important industrial commodity. Moreover, oxides of nitrogen are the major contributors to acid rain and ground-level ozone pollution. The main objective is to convert from waste to wealth by preparing nitric acid from industrial waste which is nitrogen dioxides. A photo-reactor with 1000 watt Metal Halide Lamp was used to optimize the production of nitric acid. The result from the experiment will be analyze and compared with the pure nitric acid. This method is efficient and economical.

ABSTRAK

Sebuah penyelidikan telah dilakukan untuk mempelajari teknik menghasilkan asid nitrik daripada nitrogen dioksida dengan kaedah fotokatalitik. Sehubungan dengan peningkatan pencemaran oksida nitrogen (NO_x), pengeluaran asid nitrik adalah penting dalam mengurangkan pembebasan nitrogen oksida ke atmosfera. Asid Nitrat adalah salah satu asid bukan organik yang paling penting dan sering digunakan sebagai reagen makmal dan juga penghasilan produk-produk di sektor industri. Selain itu, nitrogen dioksida adalah penyumbang utama hujan asid dan pencemaran ozon. Tujuan utama penyelidikan ini adalah untuk menukarkan bahan buangan kepada sesuatu yang lebih bernilai dengan menghasilkan asid nitrik daripada sisa industri yang tidak digunakan iaitu nitrogen dioksida. Sebuah photo reaktor bersama lampu metal halide berkuasa 1000 watt digunakan untuk mengoptimumkan pengeluaran asid nitrik. Hasil dari eksperimen akan dianalisa dan dibandingkan dengan asid nitrik tulen. Kaedah ini adalah efektif dan menjimatkan.

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LIST OF SYMBOLS

bar - pressure

FKKSA - Faculty of Chemical Engineering and Natural Resources

FT-IR - Fourier transform infrared spectroscopic

g - gram

GC-MS - gas chromatography mass spectrometer

In - inch

L - Liter

mg - milligram

Mg/l - milligram per liter

min - minute

ml/hr - millilitre per hour

mm - millimetre

Mol/g - mole per gram

°C - degree Celsius

pH - potentiometric hydrogen ion concentration

S - second

STP - Standard Temperature and Pressure

Wt% - weight percentage

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nitric acid is one of the most widely used acids in the Chemical Processing Industry. It is a key raw material in the production of ammonium nitrate for fertilizer, and is also utilized in a variety of manufacturing processes, including the production of industrial explosives, dyes, plastics, synthetic fibers, metal pickling and the recovery of uranium. As the demands on nitric acid process equipment have increased, material selection for that equipment has become crucial. Suitable structural materials need to be cost effective, reliable, durable, efficient, and non-contaminating to the product and the environment (Anarita, 1996).

Previous research which related to this topic is the Haber and Ostwald process. The commercial synthesis of ammonia began, not with the peaceful use of fertilizer, but with the necessities of war. During this period, the chemistry of ammonia synthesis was being explored by the German chemists Fritz Haber and Walther Bosch who found that it was possible to produce ammonia from nitrogen and hydrogen by the process (Anarita, 1996):-

$$N_2 + 3\ H_2 \xrightarrow{\text{iron catalyst}} 2\ NH_3$$

Previously the problem had been that N_2 is a very stable molecule, and so most attempts to convert it to less stable molecules, such as NH_3, failed because of thermodynamic or entropy problems. The secret to the Haber-Bosch process proved to be a catalyst of iron with a small amount of aluminium added (aluminium was at the time an exotic and expensive metal that probably attracted Haber's attention as a novelty) (Anarita, 1996).

Today related research for production of nitric acid from European Fertilizer Manufacturers' Association (EFMA). All plants for the production of nitric acid are currently based on the same basic chemical operations. Firstly, use oxidation of ammonia with air to give nitric oxide. Next, the process continues with the oxidation of the nitric oxide to nitrogen dioxide and absorption in water to give a solution of nitric acid (Bayless, 2007).

The efficiency of the first step is favoured by low pressure whereas that of the second is favoured by high pressure. These considerations, combined with economic reasons give rise to two types of nitric acid plant, single pressure plants and dual pressure plants. In the single pressure plant, the oxidation and absorption steps take place at essentially the same pressure. In dual pressure plants absorption takes place at a higher pressure than the oxidation stage (Evald, 2005).

Moreover, the catalyst which is used for this process are typically consists of several woven or knitted gauzes formed from wire containing about 90% platinum alloyed with rhodium for greater strength and sometimes containing palladium. Air pollution and contamination from the ammonia can poison the catalyst (Bayless, 2007).

Figure 1.1 shows the national nitrogen oxides emissions by source sector in 2002. The bar graph indicates that on road vehicles are the major contributor to emission. The emissions of nitrogen oxides (NO_x) have decreased by 31% between 1990 and 2002. In 2002, the most significant sources of NO_x emissions were the road transport sector (36%), combustion processes from within the energy industries sector (21%) and industrial energy use (15%) and the non-road transport sector (16%) (Bayless, 2007).

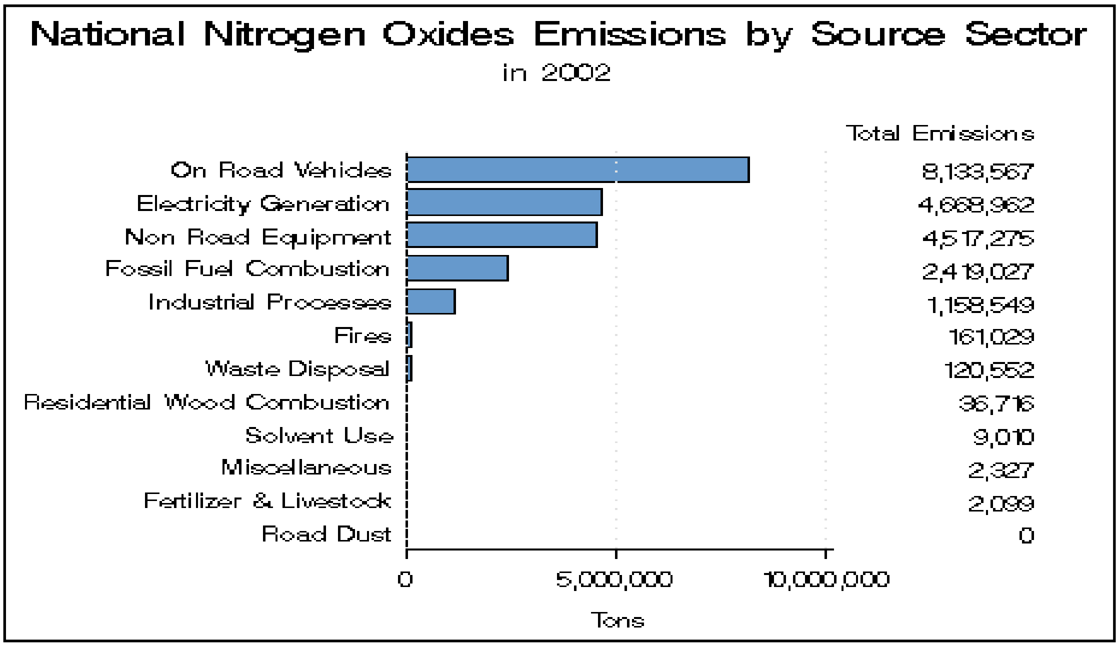

Figure 1.1: Nitrogen oxides emission by sector (Bayless, 2007).

1.2 Nitric Acid Global demand

According to Merchant Research & Consulting Ltd (UK) consulting agency, the current global market for adipic acid is pretty well supplied, and the demand for industrial chemicals has been steadily growing. The global demand for industrial chemicals based on nitric acid grows by an average of 7% per year. The production of industrial chemicals based on nitric acid, adipic acid, TDI, nitrobenzene is located mainly in Western Europe and USA, with a recent output expansion shift to eastern Asia (Aftalion, 1997).

In India, the market for concentrated nitric acid has been developing at a quick pace (7% a year). Apart from the use of concentrated nitric acid by military enterprises, this product is applied in the manufacture of nitro-aromatic compounds, acrylonitrile fibre, pesticides, medicines, pigments. The highest growth of nitric acid consumption occurs in such sectors as pharmaceuticals and pesticides (Aftalion, 1997).

The global nitric acid output tops 750-800 tons, only 15-20% of which enters the market and about 8-10% is involved in foreign trade. The remaining nitric acid is consumed by producers of nitric fertilizers, adipic acid, and other chemicals (Aftalion, 1997).

Nitric acid is a basic chemical for the manufacture of the majority of nitrogen-containing products: up to 75-80% of nitric acid is used to obtain ammonium nitrate and calcium-ammonium nitrate, carbamide-ammonium nitrates, magnesium-ammonium nitrate, as well as various nitrogenous, phosphoric and potassium fertilizers (Aftalion, 1997).

1.3 Objectives Research

The objectives of this study are:-

I. To recover NO_x recovered as nitric acid.

II. To study the effect of conversion with presence of iron (III) oxide as catalyst.

III. To study the effectiveness of photo-catalytic method.

1.4 Scope of study

There are some important tasks to be carried out in order to achieve the objective of this study. The important elements have been identified for this research in achieving the objective:

i. In this research, the method that has been chosen is photosynthesis and irradiation technique. The experiment was run in a photo-reactor with 1000 watt Metal Halide Lamp, a lamp to enhance the photosynthesis.

ii. Fourier Transform Infrared (FT-IR) will be used to analyze the product at the of the experiment.

iii. Study the effects of operating parameter such as temperature and flowrate.

1.5 Problem Statement

Nitrogen dioxide (NO_2) is the most toxic of the oxides of nitrogen. In Addition to participating in the formation of photochemical ozone at ground level, nitrogen dioxide has its own particular health effects. The acute effects of nitrogen dioxide are both direct and indirect. The direct effects are damages to the cell membranes in the lung tissues as well as constriction of the airway passages. Asthmatics are, in particular, affected by those acute effects. The indirect effects are that nitrogen dioxide causes edema, or a filling of the intercellular spaces with fluid, which may develop into local areas of infection. (Ani, 2006)

In recent research, there are several problems occur because nitric acid is corrosive to all parts of the body and contact may cause irritation, burns and necrosis. The problems that occur are equipment or piping failure because of corrosion. Besides that, there are also explosion hazard due to the air ammonia mixture and explosion of nitrite or nitrate salts (Ani, 2006).

In order to avoid certain circumstances, the solution for the problem with the recent research was found. Firstly, use stainless steel equipment to prevent corrosion. Then, air ammonia ratio is continuously controlled and kept below the hazardous range. Safety is ensured by the automatic closure of the ammonia control valve and separate shutdown trip valve when too high an air ammonia ratio is measured, either from each individual flow meter or indirectly from the catalyst gauze temperature. Any free ammonia present in the nitrous gas will give a deposit of nitrite/nitrate in a cold spot. Local washing and well proven operating practices will prevent the hazard. Besides that, this research has more advantages compare to the recent by using ‘green technology’ which is the photosynthesis process with the catalyst.

1.6 Benefit and Significance of Study

The rationale of this research is that it could encounter environmental and health problems caused by the emission of $NO_{x.}$ Besides that, this research can make used of NO_x in profitable way instead of emitting the NO_x to atmosphere. Moreover, this method would create another solution for reproducing Nitric Acid with low cost. The most vital part of this research is that it could improve and reduce pollution and change the environment towards ‘green world’.

1.7 Thesis Layout

Thesis layout is emphasizing the chapter in this research. There are generally four main chapters. In chapter 2, it will cover topics on properties and synthesis of nitric acid. Then, it will move to Ostwald and Haber process on production of nitric acid in industry. After that, came the formation of acid rain and its effect on the environment.

In chapter 3, methodology of this research is included with the material for sample preparation. It also included the experiment set up and method. This chapter will explain about the sample preparation method with can be divided into three parts. Those parts are the effect of flowrate, temperature and amount of catalyst used.

Chapter 4, focused on the result and discussion. The result of the experiment will be compared with the result from literature review and other references. If the result is valid with the literature and the optimization process is succeed, that mean our research is correct but if there are different value or result, that mean there are some mistake that had been done in this research. According to result, correction must be made to point out the mistakes. Some recommendations are also important for future researches.

Chapter 5 includes conclusion and recommendation. In this chapter, conclude all the various review and finding area in this work. Recommendation must stated in this research that can give more accurate result, using Gas Chromatography–Mass Spectrometer (GC-MS) will give the more detail component and composition of the product, and others step that can increase the accuracy of result for this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Nitric acid

Nitric acid (HNO_3), also known as aqua fortis and spirit of nitre, is a highly corrosive and toxic strong acid that can cause severe burns. Colourless when pure, older samples tend to acquire a yellow cast due to the accumulation of oxides of nitrogen. If the solution contains more than 86% nitric acid, it is referred to as fuming nitric acid. Fuming nitric acid is characterized as white fuming nitric acid and red fuming nitric acid, depending on the amount of nitrogen dioxide present (Ana, 1996). Figure 2.1 shows a sample of pure nitric acid with 100% fuming.

Figure 2.1: Pure nitric acid fuming 100%

2.2 Properties of Nitric Acid

Pure anhydrous nitric acid (100%) is a colourless liquid with a density of 1522 kg/m³ which solidifies at -42 °C to form white crystals and boils at 83 °C. When boiling in light, even at room temperature, there is a partial decomposition with the formation of nitrogen dioxide following the reaction (Sherman *et al*., 2007):

$$4\ HNO_3 \rightarrow 2\ H_2O + 4\ NO_2 + O_2\ (72°C)$$

The reaction means that anhydrous nitric acid should be stored below 0 °C to avoid decomposition. The nitrogen dioxide (NO_2) remains dissolved in the nitric acid colouring it yellow or red at higher temperatures. While the pure acid tends to give off white fumes when exposed to air, acid with dissolved nitrogen dioxide gives off reddish-brown vapours, leading to the common name "red fuming acid" or "fuming nitric acid". Fuming nitric acid is also referred to as 16-molar nitric acid — as the most concentrated form of nitric acid at Standard Temperature and Pressure (STP) (Sherman *et al*., 2007).

Nitric acid is miscible with water and distillation gives an azeotrope with a concentration of 68% HNO_3 and a boiling temperature of 120.5 °C at 1 atm, which is the ordinary concentrated nitric acid of commerce. Two solid hydrates are known; the monohydrate ($HNO_3{\cdot}H_2O$) and the trihydrate ($HNO_3{\cdot}3H_2O$). It is isoelectronic with the bicarbonate ion.

Nitrogen oxides (NO_x) are soluble in nitric acid and this property influences more or less all the physical characteristics depending on the concentration of the oxides. These mainly include the vapour pressure above the liquid and the boiling temperature, as well as the colour mentioned above (Sherman *et al*., 2007).

Nitric acid is subject to thermal or light decomposition with increasing concentration and this may give rise to some non-negligible variations in the vapour pressure above the liquid because the nitrogen oxides produced dissolve partly or completely in the acid.

2.3 The Synthesis of Nitric Acid

The NH_3 produced by the Haber process that is not used as fertilizer is burned in oxygen to generate nitrogen oxide (Dean, 1992).

$$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

Nitrogen oxide or nitric oxide, as it was once known is a colourless gas that reacts rapidly with oxygen to produce nitrogen dioxide, a dark brown gas.

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Nitrogen dioxide dissolves in water to give nitric acid and NO, which can be captured and recycled.

$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

Thus, by a three-step process developed by Friedrich Ostwald in 1908, ammonia can be converted into nitric acid.

$$4\ NH_3(g) + 5\ O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$$

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

$$3\ NO_2(g) + H_2O(l) \rightarrow 2\ HNO_3(aq) + NO(g)$$

The Haber process for the synthesis of ammonia combined with the Ostwald process for the conversion of ammonia into nitric acid revolutionized the explosives industry. Nitrates have been important explosives ever since Friar Roger Bacon mixed sulphur, saltpetre, and powdered carbon to make gunpowder in 1245 (Dean, 1992).

$$16\ KNO_3(s) + S_8(s) + 24\ C(s) \rightarrow 8\ K_2S(s) + 24\ CO_2(g) + 8\ N_2(g) \qquad H^o = -571.9\ kJ/mol\ N_2$$

Before the Ostwald process was developed the only source of nitrates for use in explosives was naturally occurring minerals such as saltpetre, which is a mixture of $NaNO_3$ and KNO_3. Once a dependable supply of nitric acid became available from the Ostwald process, a number of nitrates could be made for use as explosives. Combining NH_3 from the Haber process with HNO_3 from the Ostwald process, for example, gives ammonium nitrates, which are both an excellent fertilizer and a cheap, dependable explosive commonly used in blasting powder.

$$2\ NH_4NO_3(s) \rightarrow 2\ N_2(g) + O_2(g) + 4\ H_2O(g)$$

The destructive power of ammonia nitrate is apparent in photographs of the Alfred P. Murrah Federal Building in Oklahoma City, which was destroyed with a bomb made from ammonium nitrate on April 19, 1995 (Dean, 1992).

2.4 Industrial Preparation of Nitric Acid

Nitric acid is one of the most important inorganic acids. It is used in the production of fertilizers, dyes, drugs, and explosives. The major industrial method of producing nitric acid is the Ostwald Process. The starting materials, ammonia and molecular oxygen, are heated in the presence if a platinum-rhodium catalyst to about 800^{o}c (Considine, 1974).

2.4.1 Ostwald process

The Ostwald process is a chemical process for producing nitric acid, which was developed by Wilhelm Ostwald. It is a mainstay of the modern chemical industry. Historically and practically it is closely associated with the Haber process, which provides the requisite raw material, ammonia.

Ammonia is converted to nitric acid in two stages. It is oxidized by heating with oxygen in the presence of a catalyst such as platinum with 10% rhodium, to form nitric oxide and water (Sherman, 2007). This step is strongly exothermic, making it a useful heat source once initiated:

$$4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (g)\ (\Delta H = -950\ kJ/mol)$$

Stage two (combining two reaction steps) is carried out in the presence of water in an absorption apparatus. Initially nitric oxide is oxidized again to yield nitrogen dioxide:

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)\ (\Delta H = -114\ kJ/mol)$$

This gas is then readily absorbed by the water, yielding the desired product (nitric acid, albeit in a dilute form), while reducing a portion of it back to nitric oxide:

$$3\ NO_2\ (g) + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g)\ (\Delta H = -117\ kJ/mol)$$

The NO is recycled, and the acid is concentrated to the required strength by distillation. Alternatively, if the last step is carried out in air:

$$4\ NO_2\ (g) + O_2\ (g) + 2\ H_2O\ (l) \rightarrow 4\ HNO_3\ (aq)$$

Typical conditions for the first stage, which contribute to an overall yield of about 96%, are:

i. Pressure between 4 and 10 atmospheres (approx. 400-1010 kPa or 60-145 psig)

ii. Temperature is about 1173 K (approx. 900 °C or 1652 °F).

A complication that needs to be taken into consideration involves a side-reaction in the first step that converts the nitrogen back to N_2:

$$4\ NH_3 + 6\ NO \rightarrow 5\ N_2 + 6\ H_2O$$

This is a secondary reaction that is minimized by reducing the time the gas mixtures are in contact with the catalyst (Thieman *et al.*, 2005).

2.4.2 Haber Process

The commercial synthesis of ammonia began, not with the peaceful use of fertilizer, but with the necessities of war. In the early years of this century, Germany understood that any war that it might have with England would, at least initially, result in the blockade of critical war materials from abroad. The most important of these resources was quano, manure from seagulls that roosted along the coast of

Chile. This quano was rich in nitrates and was the basis of the German manufacture of explosives. The problem was that it had to be shipped by the tanker-load across the Atlantic and past patrolling British warships (Sherman, 2007).

But during this period, the chemistry of ammonia synthesis was being explored by the German chemists Fritz Haber and Walther Bosch who found that it was possible to produce ammonia from nitrogen and hydrogen by the process:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

Previously the problem had been that N_2 is a very stable molecule, and so most attempts to convert it to less stable molecules, such as NH_3, failed because of thermodynamic or entropy problems. The secret to the Haber-Bosch process proved to be a catalyst of iron with a small amount of aluminium added (aluminium was at the time an exotic and expensive metal that probably attracted Haber's attention as a novelty). The Haber-Bosch process operates at high pressure so as to shift the equilibrium to the right, and high temperature to increase the rates of the reaction. Of course, operating at high temperature actually shifted the reaction to the left, but the trade-off for faster rates was accepted. By removing the ammonia as liquid ammonia, the equilibrium is continuously shifted to the right (Sherman, 2007).

By 1913, the German chemical giant BASF (Badashe Analine und Soda Fabrik) had a plant operating in Ludwigshaven-Oppau, Germany making ammonia at the rate of 30 metric tons per day. Without question, this technology permitted Germany to continue making explosives and extended the war for many years. Agricultural uses: NH_3 is used to make NH_4NO_3, which is an important fertiliser, and helped to ensure the western world could grow enough food on its limited farmland areas (Sherman, 2007).

Explosives: NH_3 is oxidized to NO_2 and NO_3, which is then dissolved in water to make nitric acid. HNO_3 is the main starting reagent for most nitro-based explosives including TNT, RDX and Semtex (Sherman, 2007).

2.5 Nitrogen Cycle

The nitrogen cycle represents one of the most important nutrient cycles found in terrestrial ecosystems. Nitrogen is used by living organisms to produce a number of complex organic molecules like amino acids, proteins, and nucleic acids. The store of nitrogen found in the atmosphere, where it exists as a gas (mainly N_2), plays an important role for life (Fetzer, 1994).

This store is about one million times larger than the total nitrogen contained in living organisms. Other major stores of nitrogen include organic matter in soil and the oceans. Despite its abundance in the atmosphere, nitrogen is often the most limiting nutrient for plant growth (Fetzer, 1994).

This problem occurs because most plants can only take up nitrogen in two solid forms: ammonium ion ($NH_4^{+)}$ and the ion nitrate (NO_3^-). Most plants obtain the nitrogen they need as inorganic nitrate from the soil solution. Ammonium is used less by plants for uptake because in large concentrations it is extremely toxic. Animals receive the required nitrogen they need for metabolism, growth, and reproduction by the consumption of living or dead organic matter containing molecules composed partially of nitrogen (Fetzer, 1994).

Figure 2.2 shows a nitrogen cycle at industrial area. In most ecosystems nitrogen is primarily stored in living and dead organic matter. This organic nitrogen is converted into inorganic forms when it re-enters the biogeochemical cycle via decomposition. Decomposers, found in the upper soil layer, chemically modify the nitrogen found in organic matter from ammonia (NH_3) to ammonium salts ($NH_4^{+)}$. This process is known as mineralization and it is carried out by a variety of bacteria, actinomycetes, and fungi (Fetzer, 1994).

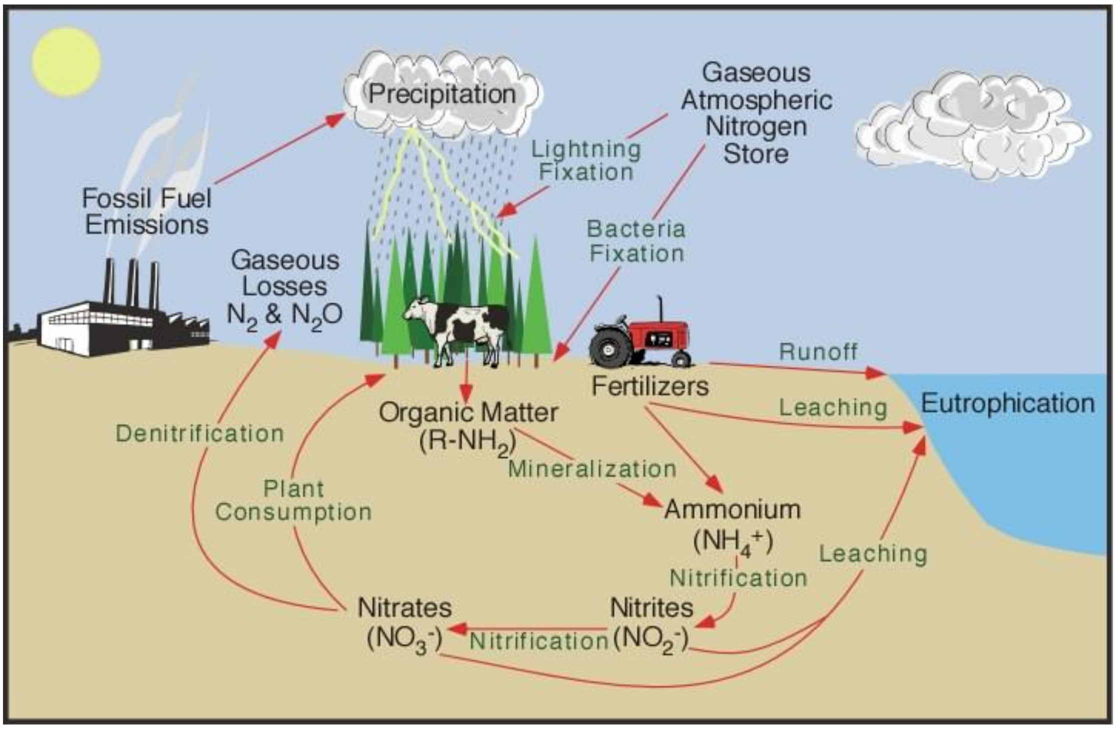

Figure 2.2: A Nitrogen cycle at industrial area

Nitrogen in the form of ammonium can be absorbed onto the surfaces of clay particles in the soil. The ion of ammonium has a positive molecular charge is normally held by soil colloids. This process is sometimes called *micelle fixation*. Ammonium is released from the colloids by way of cation exchange. When released, most of the ammonium is often chemically altered by a specific type of autotrophic bacteria (bacteria that belong to the genus Nitrosomonas) into nitrite (NO_2^-) (Fetzer, 1994).

Further modification by another type of bacteria (belonging to the genus Nitrobacter) converts the nitrite to nitrate (NO_3^-). Both of these processes involve chemical oxidation and are known as nitrification. However, nitrate is very soluble and it is easily lost from the soil system by leaching. Some of this leached nitrate flows through the hydrologic system until it reaches the oceans where it can be returned to the atmosphere by denitrification. Denitrification is also common in anaerobic soils and is carried out by heterotrophic bacteria. The process of denitrification involves the metabolic reduction of nitrate (NO_3^-) into nitrogen (N_2) or nitrous oxide (N_2O) gas. Both of these gases then diffuse into the atmosphere (Fetzer, 1994).

Almost all of the nitrogen found in any terrestrial ecosystem originally came from the atmosphere. Significant amounts enter the soil in rainfall or through the effects of lightning. The majority, however, is biochemically fixed within the soil by specialized micro-organisms like bacteria, actinomycetes, and cyanobacteria. Members of the bean family (legumes) and some other kinds of plants form mutuality symbiotic relationships with nitrogen fixing bacteria. In exchange for some nitrogen, the bacteria receive from the plants carbohydrates and special structures (nodules) in roots where they can exist in a moist environment. Scientists estimate that biological fixation globally adds approximately 140 million metric tons of nitrogen to ecosystems every year (Knight, 2004).

The activities of humans have severely altered the nitrogen cycle. Some of the major processes involved in this alteration include the application of nitrogen fertilizers to crops has caused increased rates of denitrification and leaching of nitrate into groundwater. The additional nitrogen entering the groundwater system eventually flows into streams, rivers, lakes, and estuaries. In these systems, the added nitrogen can lead to eutrophication (Knight, 2004).

The nitrogen from atmospheric sources was increasing the deposition because of fossil fuel combustion and forest burning. Both of these processes release a variety of solid forms of nitrogen through combustion.

Livestock release large amounts of ammonia into the environment from their wastes. This nitrogen enters the soil system and then the hydrologic system through leaching, groundwater flow, and runoff (Pidwirny, M. 2006).

2.6 Formation of Acid Rain

The primary cause of acid rain, more accurately called acid deposition, is air pollution from burning fossil fuels. Fossil fuel use does not directly emit acids into the atmosphere. Instead, it releases large amounts of acid precursors, primarily sulphur oxides (SOx) and nitrogen oxides (NOx). When exposed to the atmosphere, these react with water to form sulphuric acid and nitric acid, components of acid deposition (Fetzer, 1994).

Formation of acid rain by photo-catalytic oxidation is shown in Figure 2.3. Sulfur dioxide (SO^2) is emitted through combustion of fossil fuels containing sulfur as an impurity. Coal combustion is by far the major source of sulfur dioxide emitted into the atmosphere. During combustion, sulfur is oxidized to form sulfur dioxide (SO_2). Sulfur dioxide rises into the atmosphere and is oxidized once again in the presence of atmospheric hydroxyl radicals to form sulfur trioxide (SO3). Sulfur trioxide reacts with atmospheric water droplets to form sulfuric acid (H^2SO^4). Sulfur dioxide emission is the most common contributor to acid deposition, responsible for about 70% of the total. The greatest source of sulfur dioxide is electrical utility plants, which pump approximately 15 million tons of SO^2 into the atmosphere each year, out of the total 22 million tons generated annually by human activities. Other contributors of sulfur dioxide include industrial processes and automobiles and other motor vehicles (Fetzer, 1994).

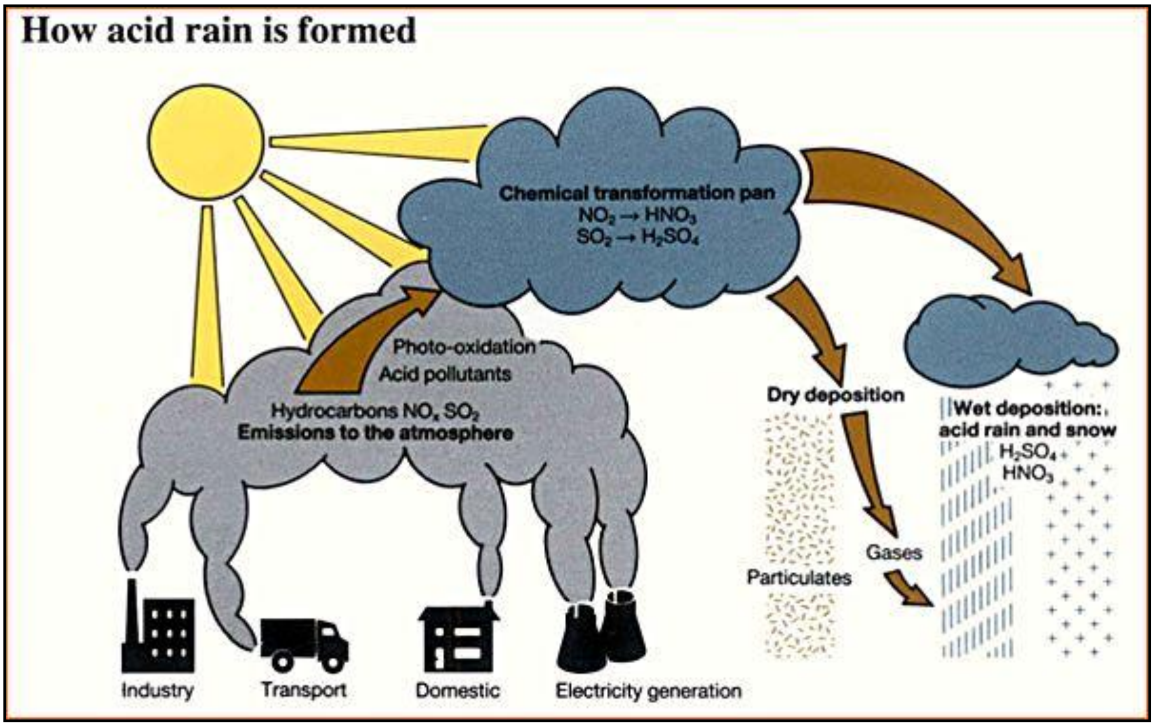

Figure 2.3: Formation of acid rain by photo-catalytic oxidation (Fetzer, 1994).

Nitrogen oxides (NO_x) are also formed through fossil fuel use. In contrast to sulfur, nitrogen is not an impurity but rather an integral part of the organic material making up fossil fuels. Fossil fuel combustion releases nitrogen into the atmosphere, usually in the form of nitric oxide (NO). Nitric oxide (NO) is oxidized by atmospheric molecules, such as ozone (O_3) or hydrogen dioxide (HO_2), to form nitrogen dioxide (NO_2). Nitrogen dioxide (NO_2) reacts with OH in the atmosphere to form nitric acid (HNO_3). Nitric acid can also form when nitrogen dioxide (NO_2) reacts with the nitrate radical (NO_3) in the presence of atmospheric water or aldehydes. Nitrogen oxides account for approximately 30% of all acid deposition. Major sources of nitrogen oxide emissions are automobiles and fossil fuel burning power stations. Nitric acid and sulfuric acid eventually fall back to the Earth's surface as acid deposition. This precipitation can be wet (rain, snow, or fog) or dry (Fetzer, 1994).

2.7 Effects of Acid Rain

The acid rain reacts chemically with any object they contact. They are corrosive in nature and has been linked to widespread environmental damage, including soil and plant degradation, depleted life in lakes and streams, and erosion of human-made structures.

2.7.1 Effects of Acid Rain on Soil

Acid rain dissolves and washes away nutrients in soil needed by plants. It dissolve toxic substances, such as aluminium and mercury, which are naturally present in some soils, freeing these toxins to pollute water or to poison plants that absorb them. The soil takes a great deal of time to develop making it a non-renewable resource. Once soil is dramatically damaged by acid, its recovery may likely take decades (Fetzer, 1994).

2.7.2 Effects of Acid Rain on Trees and Forests

Trees encounter slow growth as acid-damaged soil is unable to provide the trees the nutrients they need. Acid also damages the leaves of trees, leaving brown dead spots. Injured leaves make the tree unable to make food through photosynthesis. Once injured, trees become more prone and at risk to other threats such as cold, winter weather, insect infestations and drought (Fetzer, 1994).

2.7.3 Effects of Acid Rain on Surface Water and Marine Life

Surface water is the water found in streams, rivers and lakes. Many are close to being chemically neutral, neither acidic nor alkaline, with pH levels between 6 and 8. Acid rain falls into and drains into streams, lakes, and marshes. Toxic minerals, such as aluminium and mercury dissolved by acid rain in soil are also released to surface water poisoning aquatic life.

Acid rain has eliminated insect life and some fish species. In bodies of water with pH levels of 5, most fish eggs loose the capacity to hatch and live. Other marine organisms react negatively by decreasing in size and losing the capacity to compete for food and habitat (Fetzer, 1994).

2.7.4 Effects of Acid Rain on Plants and Animals

Aluminium dissolved by acid in soils is absorbed by roots and poisons the plant. Acid leaves brown dead spots on a plant’s leaf making it incapable of producing its own food through photosynthesis. The soil is also unable to provide it with necessary nutrients as they are already drained and washed away by the acid rain. Consequently, organisms that depend on the plant for survival are indirectly harmed. Figure 2.4 shows that visible foliar damage occurs to ivy plants treated with simulated acid rain at pH 4.0 and 3.0. The most visible damage occurred in pH 4.0. Tap water and simulated acid rain at pH 5.6 did not visibly damage the plants (Driscoll *et al*., 2003)

Figure 2.4: Ivy plants treated with simulated acid rain.

Acid rain is powerful enough to endanger an entire ecosystem. Organisms of an ecosystem are extremely interdependent and may be unable to survive without one another. A certain animal in an ecosystem that can resist acidic environment may still not survive if the animal it preys on grew less in number or have been entirely eliminated by the destructive effects of acid rain. Because of the connections between every fish, insect, plants and other kind of organisms that belong in an ecosystem, detrimental changes caused by the acid rain will affect all.

2.7.5 Effects of Acid Rain on Human Health

Toxic substances dissolved in soil by acid rain reach human water supplies. Acid interact with other chemicals in the air and create urban smog. These substances when inhaled by the lungs leads to breathing difficulties and lung irritation especially to people who already has asthma, bronchitis or other respiratory diseases. Extreme cases were premature deaths due to heart and lung disorders brought by fine acidic particles transported in long distances by the wind (Fetzer, 1994).

2.7.6 Effects of Acid Rain on Human-Made Structures

Acid rain is corrosive. It has corroded large number of buildings, structures, statues, cars and other infrastructures made with stone or metal. A number of monumental structures that is of high cultural value have been damaged irreparably to acid rain. Examples of such are the Parthenon in Athens, Greece, the Statue of Liberty in New York City and Taj Mahal in India. Dry deposition of acidic pollutants also contributes to fast dirtying of buildings and other structures making the cost of maintenance very high (Fetzer, 1994).

2.7.7 Effects of Acid Rain – Global Warming

Acid rain has one remarkably beneficial effect. It slows down global warming. It increases in the average temperature of the Earth’s atmosphere, oceans and landmasses due to the greenhouse gases. Greenhouse Gases such as Carbon dioxide, methane and nitrous oxide are examples of such gases that trap heat. They have rapidly increased in great percentages making the atmosphere too thick with heat trapping gases and causing gradual changes in the world’s climate (Fetzer, 1994).

Sulphur pollution in the atmosphere mitigates the production of methane which released to the atmosphere through coal mining. It also found in live plants, rice paddies, wetlands, and other animals such as cows. It traps thirty times more heat than carbon dioxide does. Sulphur eating bacteria have been discovered in wetlands where there are microbes, the biggest producers of methane. Sulphur-eating bacteria from sulphur deposits reduce methane release by 18-15% (Fetzer, 1994).

2.8 Reducing Formation of Acid Rain

Oxides of nitrogen are one of the causes for formation of acid rain. Figure 2.5 shows clean smokestacks as industrial chimneys to reduce the formation of acid rain. The process use of Flue Gas Desulphuration (FGD) for installations of scrubbers which are liquid-like filters in chimney towers that push exhausts gas with sprays of calcium hydroxide or water containing lime. Lime reacts with sulphur dioxide and transforms it into calcium sulphate which is pH-neutral and solid in form. These solid calcium sulphates are then disposed to landfills or sold to chemical companies as gypsum. Gypsums may be used as cement, plaster and fertilizers (King, 2008).

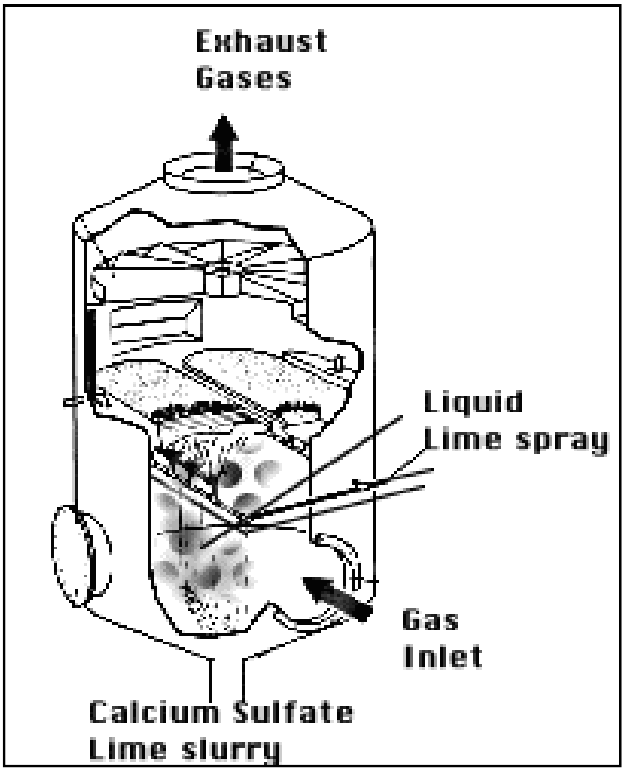

Figure 2.5: Clean smokestacks as industrial chimneys.

Besides that, using alternative mode of transportation could also reduce the acid rain. Transportation vehicles are one of the major sources of pollutants that form acid rain. Hence, taking public transportation or carpooling could decreases number of transport on the road. Moreover, walking or riding bicycles is a good alternative as well. Vehicles should be properly maintained to reduce the pollution release by the exhaust. Lastly, buy vehicles with low nitrogen oxide emissions is one of better option.

In addition, using alternative sources of energy could also reduce the pollution. There are other sources that are less environmentally harmful such as nuclear power, hydropower, wind energy, geothermal energy and solar energy. Some of these alternatives are more expensive to produce however advancements in technologies may decrease monetary cost in the future.

Furthermore, one of the alternative ways is by restoring damaged environment. Liming is the use of limestone in acidic lakes to neutralize the acidity in water. This technique is a short-term remedy but it could allow organisms in soil or aquatic animals to remain in water and survive until acid deposits have been totally washed out of the area. An expensive method and has to be done repeatedly on the damaged places to yield desirable results (Son *et al.*, 2004).

People must understand how acid rain damages the environment and know what changes could be made to pollution sources. Knowledge would bring concern and discipline and would help people make right decisions on how to control and reduce acid rain.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This research is mainly about preparing nitric acid from nitrogen dioxides by using photo-catalytic method. A 1000 watt metal halide lamp is used to enhance the reaction by using it intensity. Moreover, this research is totally new research and has lack of references related to this research. Several parameters have been manipulated in order to analyze the sample of the product.

3.2 Material for Sample Preparation

For this experiment, nitrogen dioxide with minimum purity 99.5% (Liquid Phase) as shown in figure 3.1 was used. The gas cylinder was ordered five month earlier from Malaysia Oxygen (MOX). Nitrogen dioxides (NO_2) also well known as dinitrogen tetroxide or nitrogen peroxide and of them could be included in oxides of nitrogen group. There several emergency overview need to be aware to avoid further circumstances. Nitrogen dioxides are poisonous and gas under pressure which may be fatal if inhaled.

Figure 3.1: Cylinders of nitrogen dioxides (NO_2) with purity 99.5%

The catalyst used for the experiment, iron (III) oxides also known as ferric oxide was available at FKKSA laboratory. This material is considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).

3.3 Experiment Set Up and Method

Figure 3.2 shows a photo-reactor which needs to be setup in order to run the experiment. First of all, the 1000 watt metal halide lamp must be prepared and installed under the quartz glass reaction vessel. After that, the nitrogen dioxides cylinder must be attached with pressure gauge and flow meter as well. Furthermore, the high speed stirring motor were connected to the fluid sealed stirring device. A thermocouple was installed to the vessel to inspect the temperature of the solvent during the experiment.

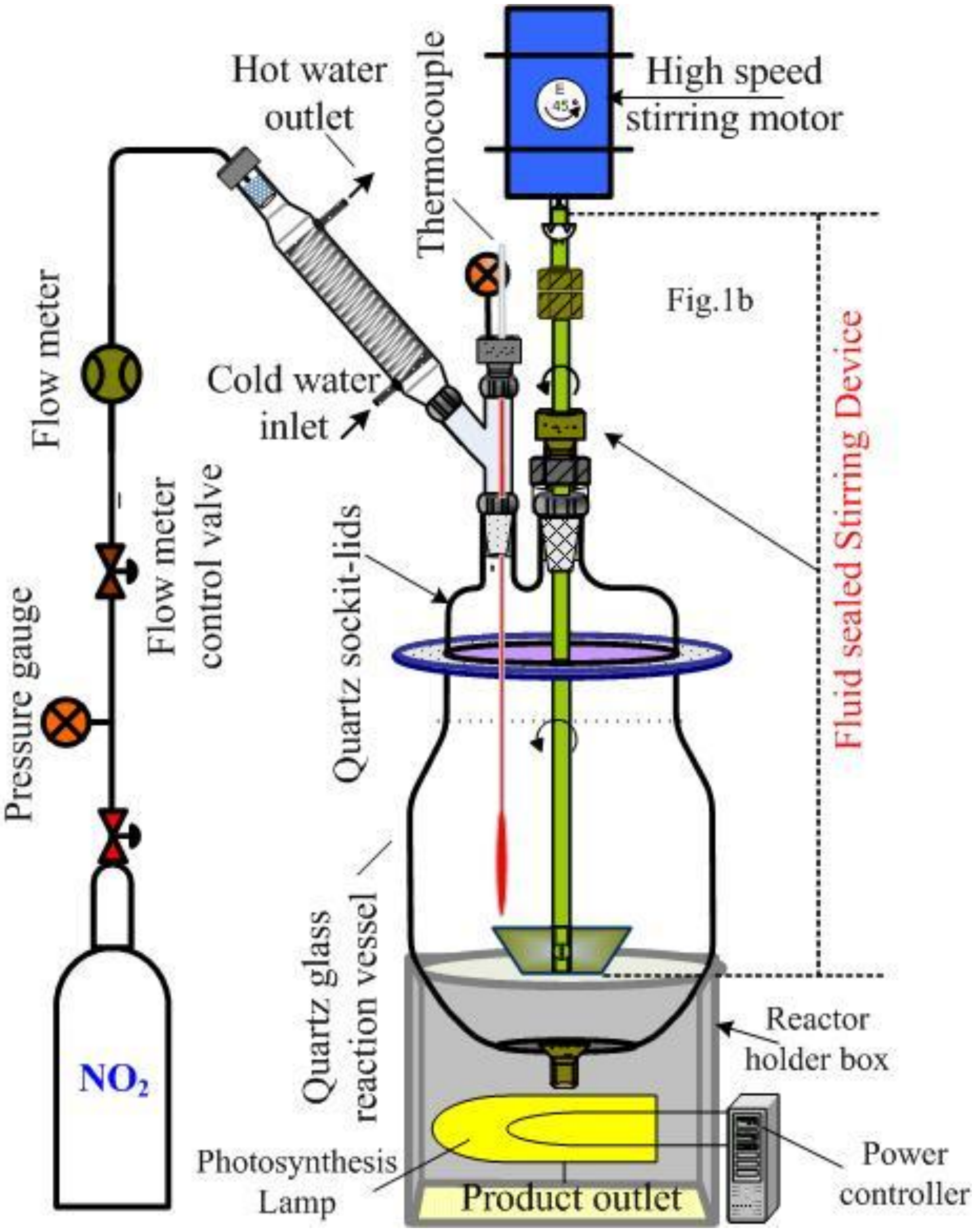

Figure 3.2: Experimental setup of a photo-reactor

After all the equipment has been setup, a gas leak test was run supervise by the experienced laboratory technician for purpose of safety by using soap bubbles as shown in figure 3.3. The first thing you will want to do is shut the main gas supply off. You can do this by turning off the main valve at the meter. Attach the tester by means of whatever fittings it will take to attach the pressure gauge. Attach a fitting to the gas pipe so you can pump it up with air. Watch the gauge you will only need to have 5 psi to test the system. Watch the gauge. If the gauge falls below 5 psi there is a leak. You can go around and spray all the joints with the soapy solution. If the solution bubbles up that is where the leak is. Repair the leak by disassembling the fittings and using pipe joint compound certified for gas. Apply the compound to the male treads only. Reinstall the fittings and retest.

Figure 3.3: Gas leak test by using soap bubbles.

3.4 Sample Preparation Method

There are many type of catalyst could be used for this experiment but the only available catalyst in the laboratory is iron (III) oxide which is also one of the best catalyst for the experiment. Firstly, prepare 10 mg of iron (III) oxide catalyst and placed into the quartz glass reaction vessel. After that, prepare a 1.4 L of diluted water and poured into the vessel as well.

3.4.1 Effect of Flowrate on Nitric Acid Production

The pressure gauge must be open but should not exceed 2 bars because the photo-reactor could not withstand higher pressure. After that, the flow meter was adjusted to 20 ml/hr. The metal halide lamp and high speed stirring motor was turn on. The experiment was run for 2 hours, and then the samples were collected to analyze. The experiment was repeated by using flowrate of 40, 60, 80, and 100 ml/hr.

3.4.2 Effect of Temperature on Nitric Acid Production

The photo-reactor has to undergo some modification in order to place the quartz glass reaction vessel into a water bath. Figure 3.4 shows a laboratory water bath is a tool used to maintain a very stable temperature much like an incubator. Water baths can hold often temperatures within a tenth of a degree Celsius. The water is often circulated and sometimes beads are used as an alternative waterless option.

Figure 3.4: A Water Bath with temperature regulator

For the experiment, prepare 10 ml/hr of iron (III) oxide and placed into the quartz glass reaction vessel. After that, prepare a 1.4 L of diluted water and poured into the vessel as well. Then, the flow meter was adjusted to 20 ml/hr. The metal halide lamp and high speed stirring motor was turn on. Next, set the temperature on the water bath panel to 20ºC. The experiment was run for 2 hours, and then the samples were collected to analyze. The experiment was repeated by using different temperature which is 40, 60 and 80ºC.

3.5 FT-IR Analysis Procedure

Fourier Transform Infrared Spectroscopy (FT-IR) uses infrared light to create an infrared absorption spectrum for identifying types of chemical bonds in a molecule. The spectrum acts like a molecular “fingerprint”. FT-IR is most useful for identifying chemicals that are either organic or inorganic. The analysis can be applied to solids, liquids or gases. FT-IR analysis of nitric acid was performed to determine its functional groups.

Place a small drop of the compound on one of the KBr plates. Place the second plate on top and make a quarter turn to obtain a nice even film. Place the plates into the sample holder and run a spectrum. If the sample is too concentrated, separate the plates and wipe one side clean before putting them back together.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of futurre samples. Wipe the windows with a tissue, then wash several times with methylene chloride, then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Experimental Result

Figure 4.1 shows the samples of nitric acid product after the experiment and already been cooled down. Iron (III) oxide has already been at the bottom of the beaker after the cooling. Hence, it is easier to collect the sample because the product and precipitate are separated.

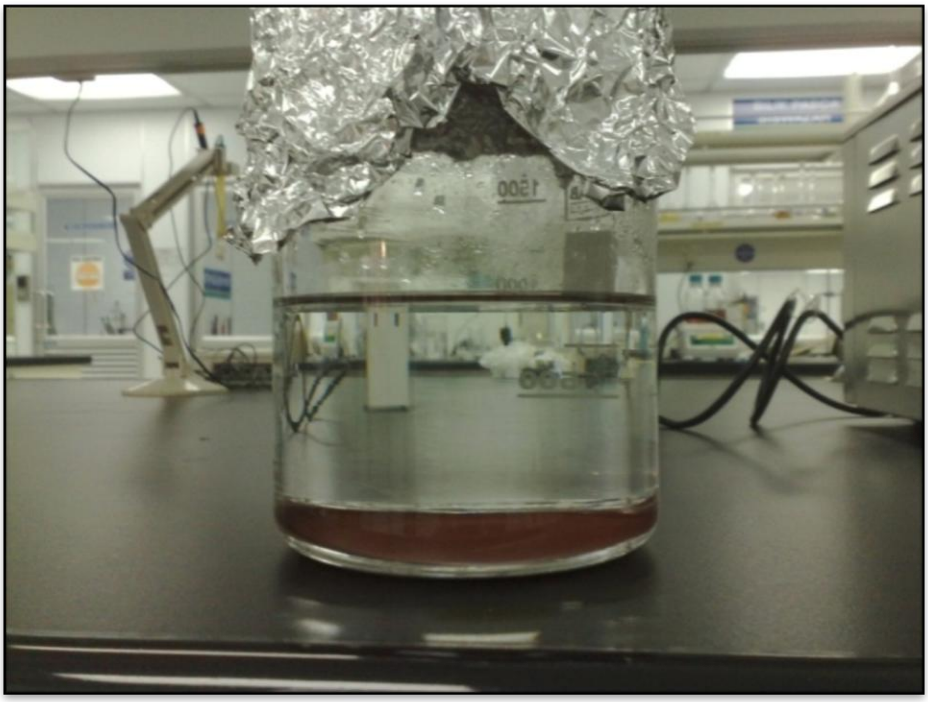

Figure 4.1: Sample of nitric acid product

Meanwhile, figure 4.2 shows the samples of catalyst, Iron (III) Oxide used for this experiment. Rust is often called iron (III) oxide, and to some extent, this label is useful, because rust shares several properties and has a similar composition. To a chemist, rust is considered an ill-defined material, described as hydrated ferric oxide.

Figure 4.2: Iron (III) oxide, catalyst for nitric acid production

4.2 Effect of Flowrate on Nitric Acid Production

The experiment was run with different flowrate which is 20, 40, 60, 80 and 100 ml/hr as shown in figure 4.3. An external flowrate meter was attached to meter gauge to adjust the flowrate to 1 bar. After that, gas leak test was run for safety purposes.

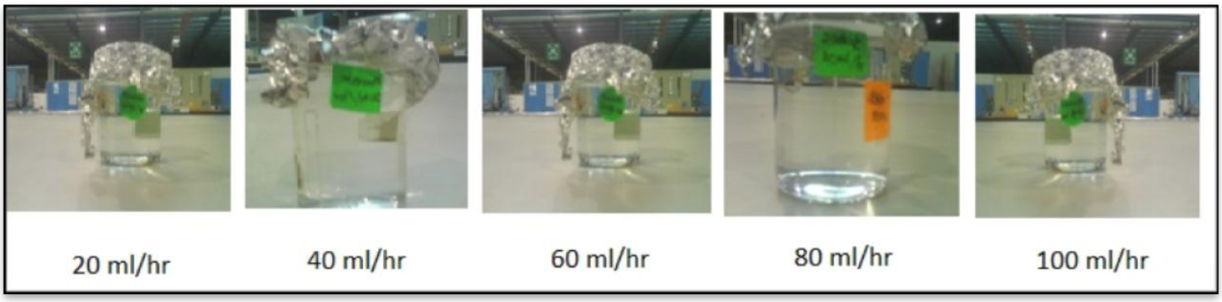

Figure 4.3: Sample of nitric acid with difference flowrate

The pH level of Nitric acid is 3; however it has been concentrated for safety issues so it has a pH level of 4-5. The result for the experiment of reading pH with different flowrate was shown in table 4.1.

Figure 4.4 shows that the pH is directly proportional with increasing of flowrate. It is because 20 ml/hr is the maximum flowrate needed for the reaction. Flowrate more than 20 ml/hr would be excess to the reaction and decrease the pH of the product. The experiment should be run using lower flowrate to find the maximum flowrate. Unfortunately, the only available flowrate meter in the laboratory has minimum reading of 20 ml/hr.

Table 4.1: Result for pH reading with different flowrate

Flow rate of NO_2 (ml/hr)	**pH**
20	3.55
40	3.89
60	4.22
80	4.74
100	5.13

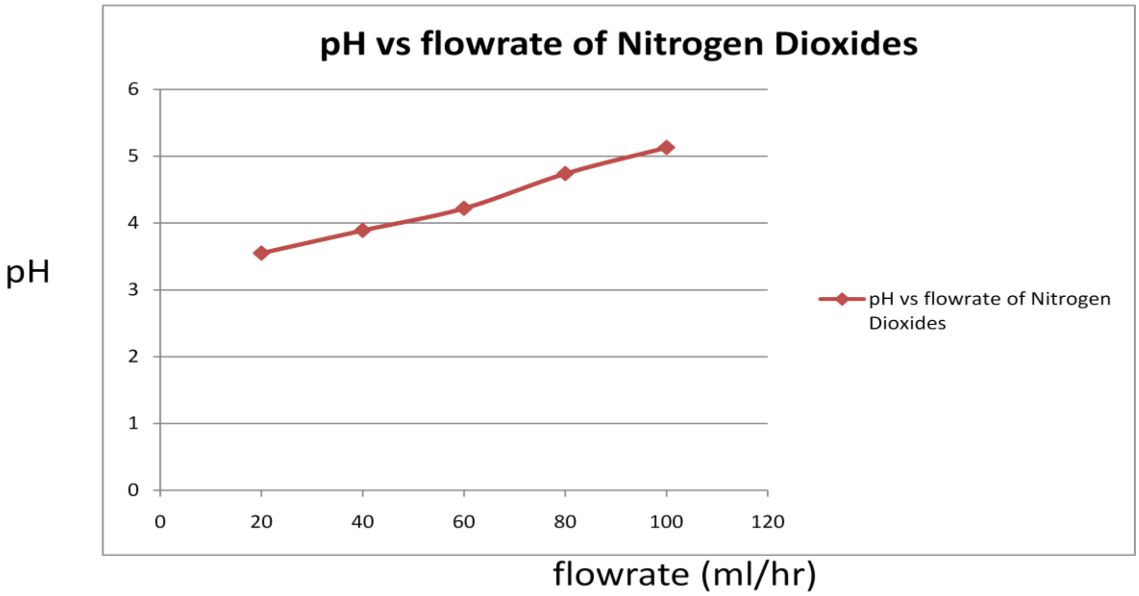

Figure 4.4: Flowrate effect on the pH of nitric acid

4.3 Effect of temperature on Nitric Acid Production

Temperatures play a major role as one of the main parameter for this experiment. Water bath was used because it can increase or decrease the temperature of the solution of nitric acid. The experiment was run by different temperature which is 20ºC, 40 ºC, 60 ºC, and 80 ºC. The result for reading of pH with different temperature was shown in table 4.2.

Table 4.2: Result for reading of pH with different temperature.

Temperature (ºC)	pH
20	5.46
40	5.18
60	3.84
80	3.72

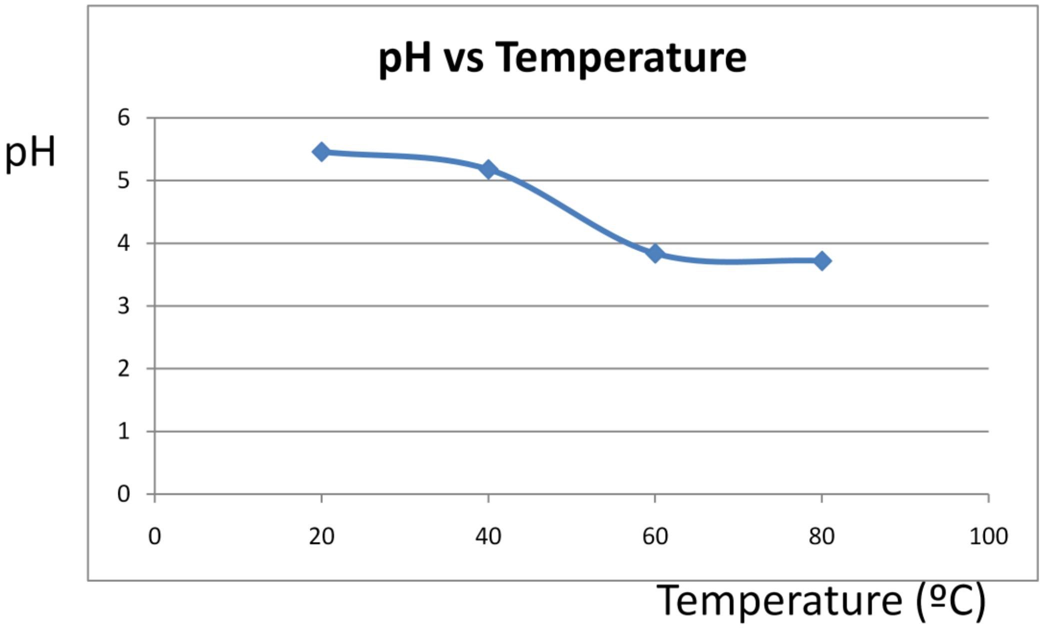

Figure 4.5: Temperature effect on the pH of nitric acid

Figure 4.5 shows that 60ºC is the optimum temperature for the reaction to occur because the acidity of nitric acid become constant after 60ºC. The experiment must be run constantly with temperature more than 60ºC because temperature below 60ºC will not produce a nitric acid.

4.4 Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared (FTIR) was used in this analysis in order to determine the functional of the product. The functional groups of nitric acid will be determined based on the peak value from the graph shown in Figure 4.6. The optimum product of nitric acid was chosen which is product from 20 ml/hr flowrate with temperature 60ºC. The wave number of the functional group represents the functional group in the product. The functional group of the product was analyzed by determined the wavelength in the graph and compared to the references. Each of the group has their own wave length. The peak for nitric acid which is from nitro group was referred from journals as shown in Table 4.3 is 1550 cm^{-1}. Meanwhile, the reading of wavelength for the nitric acid product is 1644.69 cm^{-1} which is near and still in the range of nitro functional group.

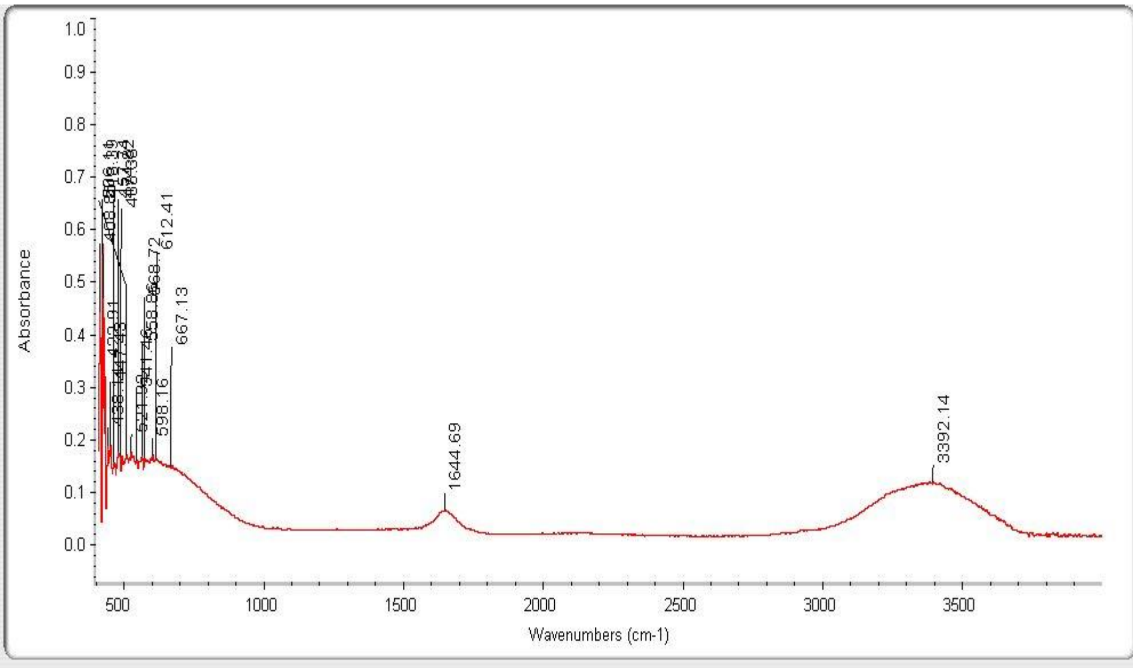

Figure 4.6: FT-IR of nitric acid product

Table 4.3: Characteristic of adsorptions by functional class

Functional Class	Characteristic Absorptions
Sulfur Functions	
S-H thiols	2550-2600 cm^{-1} (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)
C=S thiocarbonyl	1050-1200 (str)
S=O sulfoxide sulfone sulfonic acid sulfonyl chloride sulfate	1030-1060 (str) 1325± 25 (as) & 1140± 20 (s) (both str) 1345 (str) 1365± 5 (as) & 1180± 10 (s) (both str) 1350-1450 (str)
Phosphorous Functions	
P-H phosphine	2280-2440 cm^{-1} (med & shp) 950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)
P=O phosphine oxide phosphonate phosphate phosphoramide	1100-1200 (str) 1230-1260 (str) 1100-1200 (str) 1200-1275 (str)

Silicon Functions	
Si-H silane	2100-2360 cm^{-1} (str)
Si-OR	1000-11000 (str & brd)
Si-CH$_3$	1250± 10 (str & shp)
Oxidized Nitrogen Functions	
=NOH oxime O-H (stretch) C=N N-O	 3550-3600 cm^{-1} (str) 1665± 15 945± 15
N-O amine oxide aliphatic aromatic	 960± 20 1250± 50
N=O nitroso nitro	1550± 50 (str) 1530± 20 (as) & 1350± 30 (s)

Another FT-IR test was run by using a pure nitric acid as a standard sample to compare with the product from the experiment. Figure 4.7 show that the peak for both nitric acid product and standard sample has almost the same peak. Furthermore, both of the peaks are still in the range of nitro functional class which is 1500 -1700 cm^{-1}.

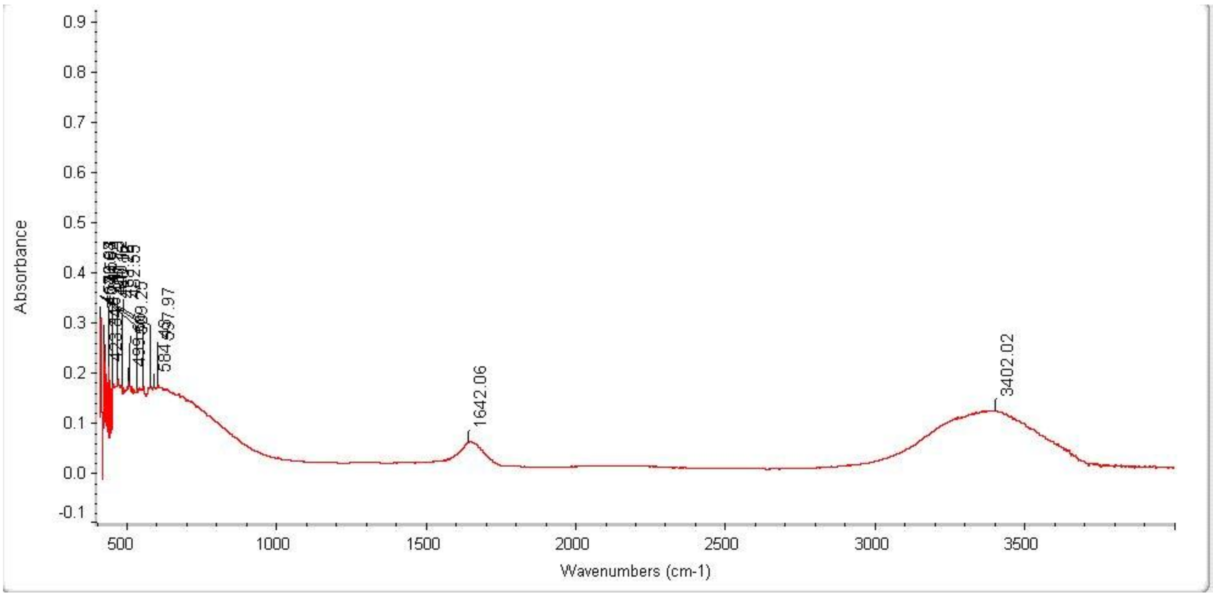

Figure 4.7: FT-IR of standard nitric acid

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

Based on the result in this research, it shows that the objective of this research is achieved. The main objective of this research is to recover NO_x recovered as nitric acid. Other objectives are to study the effect of conversion with presence of iron (III) oxide as catalyst as well as to study the effectiveness of photo-catalytic method.

At the beginning, the research did not progress as expected. However, after the research had been done, a lot of challenge had to be faced in order to achieve the objective of this study. Some of the problem is to install the 1000 watt metal halide lamp to the photo-reactor which needs a lot of adjustment and the reactor has to be calibrating again.

It could be concluded that this research is one of the solution to reduce the amount of oxides of nitrogen emitted to the atmosphere by reproducing them into nitric acid using photo-catalytic method. Furthermore, this method is economical and can be commercialize in many industries because they are highly demanded these days.

5.2 Recommendation

Based on the result and discussion, these recommendations can be taken into consideration to upgrade future studies of nitric acid production:-

i. Analyze the product by using Gas Chromatography – Mass Spectrometer (GC-MS) will give the more detail component of the product.

ii. Use more proper reactor which can withstand higher pressure.

iii. Use different type of catalyst such as titanium dioxide (TiO_2), activated carbon (AC) and ferric oxide (Fe_2O_3).

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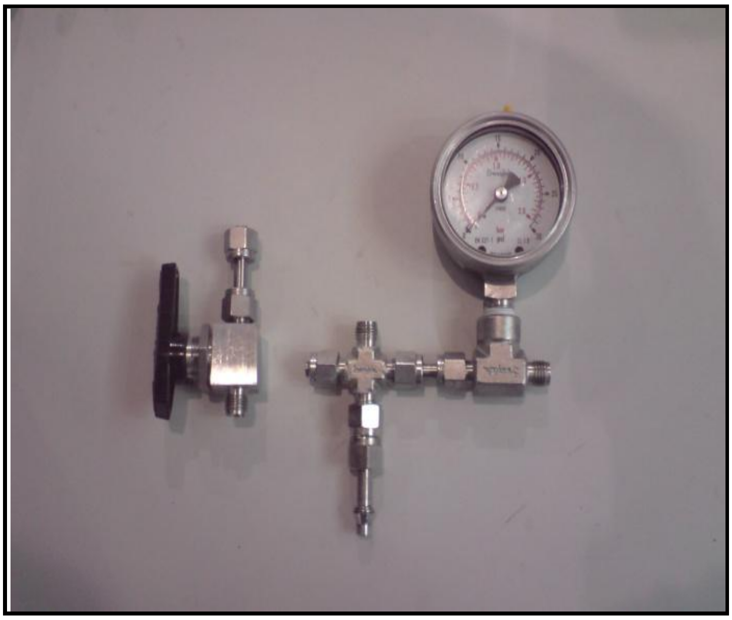
APPENDIX A

EXPERIMENT PICTURES

Picture 1: 1000 watt HPI-T metal halide lamp



Picture 2: Valve and pressure gauge

Picture 3: Nitrogen dioxides cylinder with water bath (blue tank)

Picture 4: Fourier Transform Infrared Spectroscopy (FT-IR)

A PREPARATION OF NITRIC ACID FROM NITROGEN DIOXIDES USING PHOTOCATALYTIC METHOD

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Abstract

A research is conducted to study on preparation of nitric acid from nitrogen dioxides using photocatalytic method. Due to the increasing pollution of oxides of nitrogen (NO_x), production of nitric acid is vital in reducing the oxides of nitrogen release to the atmosphere. Nitric acids are one of the most important inorganic acids and commonly used as laboratory reagent and an important industrial commodity. Moreover, oxides of nitrogen are the major contributors to acid rain and ground-level ozone pollution. The main objective is to convert from waste to wealth by preparing nitric acid from industrial waste which is nitrogen dioxides. A photo-reactor with 1000 watt Metal Halide Lamp was used to optimize the production of nitric acid. The result from the experiment will be analyze and compared with the pure nitric acid. This method is efficient and economical.

Abstrak

Sebuah penyelidikan telah dilakukan untuk mempelajari teknik menghasilkan asid nitrik daripada nitrogen dioksida dengan kaedah fotokatalitik. Sehubungan dengan peningkatan pencemaran oksida nitrogen (NO_x), pengeluaran asid nitrik adalah penting dalam mengurangkan pembebasan nitrogen oksida ke atmosfera. Asid Nitrat adalah salah satu asid bukan organik yang paling penting dan sering digunakan sebagai reagen makmal dan juga penghasilan produk-produk di sektor industri. Selain itu, nitrogen dioksida adalah penyumbang utama hujan asid dan pencemaran ozon. Tujuan utama penyelidikan ini adalah untuk menukarkan bahan buangan kepada sesuatu yang lebih bernilai dengan menghasilkan asid nitrik daripada sisa industri yang tidak digunakan iaitu nitrogen dioksida. Sebuah photo reaktor bersama lampu metal halide berkuasa 1000 watt digunakan untuk mengoptimumkan pengeluaran asid nitrik. Hasil dari eksperimen akan dianalisa dan dibandingkan dengan asid nitrik tulen. Kaedah ini adalah efektif dan menjimatkan.

Keywords: nitric acid (HNO_3); nitrogen dioxides (NO_2); photocatalytic; Metal Halide Lamp.

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1. Introduction

Nitric acid is one of the most widely used acids in the Chemical Processing Industry. It is a key raw material in the production of ammonium nitrate for fertilizer, and is also utilized in a variety of manufacturing processes, including the production of industrial explosives, dyes, plastics, synthetic fibres, metal pickling and the recovery of uranium. As the demands on nitric acid process equipment have increased, material selection for that equipment has become crucial. Suitable structural materials need to be cost effective, reliable, durable, efficient, and non-contaminating to the product and the environment (Anarita, 1996).

Previous research which related to this topic is the Haber and Ostwald process. The commercial synthesis of ammonia began, not with the peaceful use of fertilizer, but with the necessities of war. During this period, the chemistry of ammonia synthesis was being explored by the German chemists Fritz Haber and Walther Bosch who found that it was possible to produce ammonia from nitrogen and hydrogen by the process (Anarita, 1996):-

$$N_2 + 3\,H_2 \xrightarrow{\text{iron catalyst}} 2\,NH_3$$

Previously the problem had been that N_2 is a very stable molecule, and so most attempts to convert it to less stable molecules, such as NH_3, failed because of thermodynamic or entropy problems. The secret to the Haber-Bosch process proved to be a catalyst of iron with a small amount of aluminium added (aluminium was at the time an exotic and expensive metal that probably attracted Haber's attention as a novelty) (Anarita, 1996).

Today related research for production of nitric acid from European Fertilizer Manufacturers' Association (EFMA). All plants for the production of nitric acid are currently based on the same basic chemical operations. Firstly, use oxidation of ammonia with air to give nitric oxide. Next, the process continues with the oxidation of the nitric oxide to nitrogen dioxide and absorption in water to give a solution of nitric acid (Bayless, 2007).

The efficiency of the first step is favoured by low pressure whereas that of the second is favoured by high pressure. These considerations, combined with economic reasons give rise to two types of nitric acid plant, single pressure plants and dual pressure plants. In the single pressure plant, the oxidation and absorption steps take place at essentially the same pressure. In dual pressure plants absorption takes place at a higher pressure than the oxidation stage (Evald, 2005).

Moreover, the catalyst which is used for this process are typically consists of several woven or knitted gauzes formed from wire containing about 90% platinum alloyed with rhodium for greater strength and sometimes containing palladium. Air pollution and contamination from the ammonia can poison the catalyst (Bayless, 2007).

2. Experimental

2.1 Introduction

This research is mainly about preparing nitric acid from nitrogen dioxides by using photo-catalytic method. A 1000 watt metal halide lamp is used to enhance the reaction by using it intensity. Moreover, this research is totally new research and has lack of references related to this research. Several parameters have been manipulated in order to analyze the sample of the product.

2.2 Material for Sample Preparation

For this experiment, nitrogen dioxide with minimum purity 99.5% (Liquid Phase) was used. The gas cylinder was ordered five month earlier from Malaysia Oxygen (MOX). Nitrogen dioxides (NO_2) also well known as dinitrogen tetroxide or nitrogen peroxide and of them could be included in oxides of nitrogen group. There several emergency overview need to be aware to avoid further circumstances. Nitrogen dioxides are poisonous and gas under pressure which may be fatal if inhaled. The catalyst used for the experiment, iron (III) oxides also known as ferric oxide was available at FKKSA laboratory. This material is considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).

2.3 Experiment Set Up and Method

First of all, the 1000 watt metal halide lamp must be prepared and installed under the quartz glass reaction vessel. After that, the nitrogen dioxides cylinder must be attached with pressure gauge and flow meter as well. Furthermore, the high speed stirring motor were connected to the fluid sealed stirring device. A thermocouple was installed to the vessel to inspect the temperature of the solvent during the experiment.

After all the equipment has been setup, a gas leak test was run supervise by the experienced laboratory technician for purpose of safety by using soap bubbles. The first thing you will want to do is shut the main gas supply off. You can do this by turning off the main valve at the meter. Attach the tester by means of whatever fittings it will take to attach the pressure gauge. Attach a fitting to the gas pipe so you can pump it up with air. Watch the gauge you will only need to have 5 psi to test the system. Watch the gauge. If the gauge falls below 5 psi there is a leak. You can go around and spray all the joints with the soapy solution. If the solution bubbles up that is where the leak is. Repair the leak by disassembling the fittings and using pipe joint compound certified for gas. Apply the compound to the male treads only. Reinstall the fittings and retest.

2.4 Sample Preparation Method

There are many type of catalyst could be used for this experiment but the only available catalyst in the laboratory is iron (III) oxide which is also one of the best catalyst for the experiment. Firstly, prepare 10 mg of iron (III) oxide catalyst and placed into the quartz glass reaction vessel. After that, prepare a 1.4 L of diluted water and poured into the vessel as well.

2.4.1 Effect of Flowrate on Nitric Acid Production

The pressure gauge must be open but should not exceed 2 bars because the photo-reactor could not withstand higher pressure. After that, the flow meter was adjusted to 20 ml/hr. The metal halide lamp and high speed stirring motor was turn on. The experiment was run for 2 hours, and then the samples were collected to analyze. The experiment was repeated by using flowrate of 40, 60, 80, and 100 ml/hr.

2.4.2 Effect of Temperature on Nitric Acid Production

The photo-reactor has to undergo some modification in order to place the quartz glass reaction vessel into a water bath. Water baths can hold often temperatures within a tenth of a degree Celsius. The water is often circulated and sometimes beads are used as an alternative waterless option.

For the experiment, prepare 10 ml/hr of iron (III) oxide and placed into the quartz glass reaction vessel. After that, prepare a 1.4 L of diluted water and poured into the vessel as well. Then, the flow meter was adjusted to 20 ml/hr. The metal halide lamp and high speed stirring motor was turn on. Next, set the temperature on the water bath panel to 20ºC. The experiment was run for 2 hours, and then the samples were collected to analyze. The experiment was repeated by using different temperature which is 40, 60 and 80ºC.

2.5 FT-IR Analysis Procedure

Fourier Transform Infrared Spectroscopy (FT-IR) uses infrared light to create an infrared absorption spectrum for identifying types of chemical bonds in a molecule. The spectrum acts like a molecular “fingerprint”. FT-IR is most useful for identifying chemicals that are either organic or inorganic. The analysis can be applied to solids, liquids or gases. FT-IR analysis of nitric acid was performed to determine its functional groups.

Place a small drop of the compound on one of the KBr plates. Place the second plate on top and make a quarter turn to obtain a nice even film. Place the plates into the sample holder and run a spectrum. If the sample is too concentrated, separate the plates and wipe one side clean before putting them back together.

The KBr plates must be thoroughly cleaned after this procedure to prevent contamination of futurre samples. Wipe the windows with a tissue, then wash several times with methylene chloride, then ethanol. Use the polishing kit in the lab to polish the window surface. Wear gloves to prevent fogging. The cleaned surface should be clear and free from scratches.

3. Result and discussion

3.1 Experimental Result

Figure 1 shows the samples of nitric acid product after the experiment and already been cooled down. Iron (III) oxide has already been at the bottom of the beaker after the cooling. Hence, it is easier to collect the sample because the product and precipitate are separated.

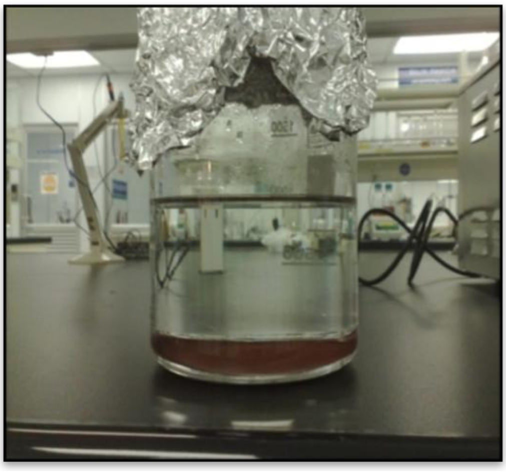

Figure 3.1: Sample of nitric acid product

3.2 Effect of Flowrate on Nitric Acid Production

The experiment was run with different flowrate which is 20, 40, 60, 80 and 100 ml/hr. An external flowrate meter was attached to meter gauge to adjust the flowrate to 1 bar. After that, gas leak test was run for safety purposes. The pH level of Nitric acid is 3; however it has been concentrated for safety issues so it has a pH level of 4-5. Figure 3.2 shows that the pH is directly proportional with increasing of flowrate. It is because 20 ml/hr is the maximum flowrate needed for the reaction. Flowrate more than 20 ml/hr would be excess to the reaction and decrease the pH of the product. The experiment should be run using lower flowrate to find the maximum flowrate. Unfortunately, the only available flowrate meter in the laboratory has minimum reading of 20 ml/hr.

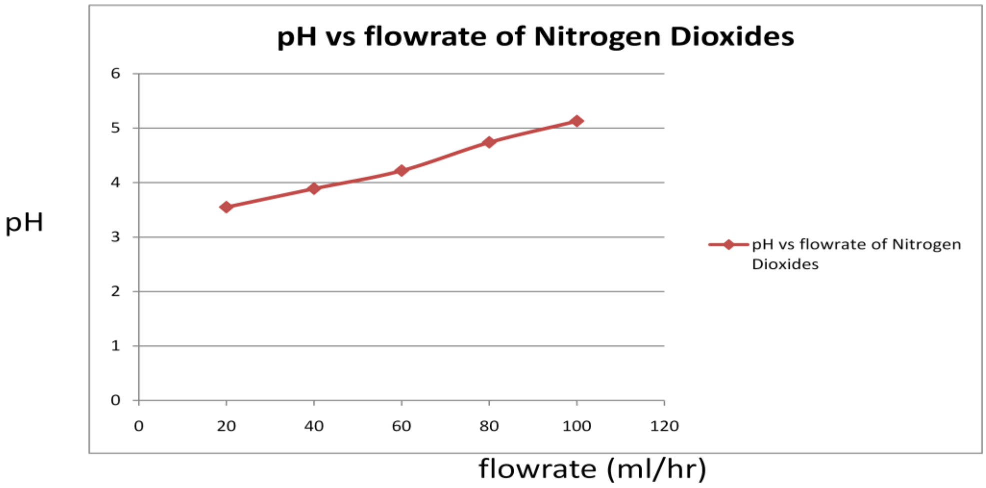

Figure 3.2: Flowrate effect on the pH of nitric acid

3.3 Effect of temperature on Nitric Acid Production

Temperatures play a major role as one of the main parameter for this experiment. Water bath was used because it can increase or decrease the temperature of the solution of nitric acid. The experiment was run by different temperature which is 20ºC, 40 ºC, 60 ºC, and 80 ºC. Figure 3.3 shows that 60ºC is the optimum temperature for the reaction to occur because the acidity of nitric acid become constant after 60ºC. The experiment must be run constantly with temperature more than 60ºC because temperature below 60ºC will not produce a nitric acid.

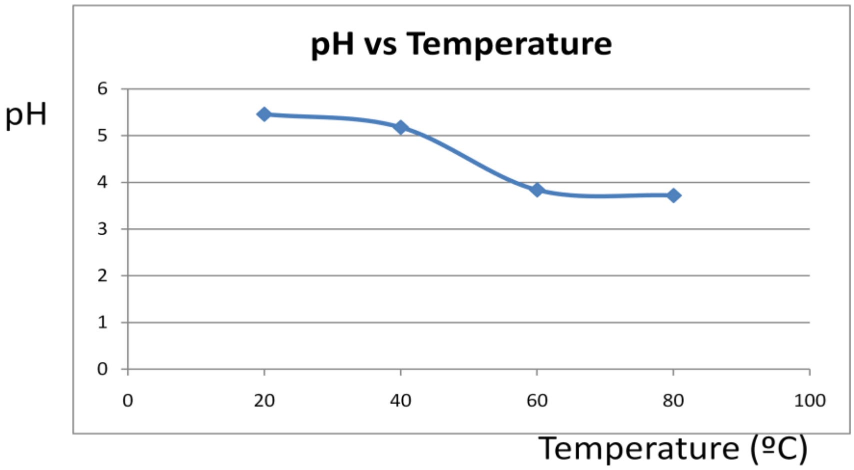

Figure 3.3: Temperature effect on the pH of nitric acid

4.4 Fourier Transform Infrared (FTIR) Analysis

Fourier transform infrared (FTIR) was used in this analysis in order to determine the functional of the product. The functional groups of nitric acid will be determined based on the peak value from the graph shown in figure 3.4. The optimum product of nitric acid was chosen which is product from 20 ml/hr flowrate with temperature 60ºC. The wave number of the functional group represents the functional group in the product. The functional group of the product was analyzed by determined the wavelength in the graph and compared to the references. Each of the group has their own wave length. The peak for nitric acid which is from nitro group was referred from journals as shown in Table 3.1 is 1550 cm^{-1}. Meanwhile, the reading of wavelength for the nitric acid product is 1644.69 cm^{-1} which is near and still in the range of nitro functional group.

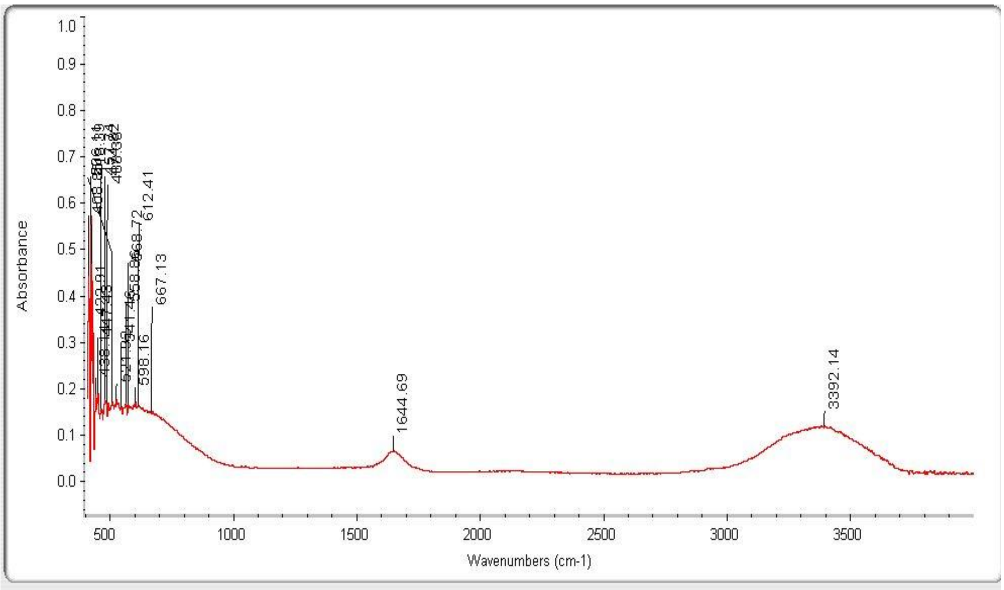

Figure 3.4: FT-IR of nitric acid product

Table 3.1: Characteristic of adsorptions by functional class

Oxidized Nitrogen Functions	
=NOH oxime O-H (stretch) C=N N-O	 3550-3600 cm^{-1} (str) 1665± 15 945± 15
N-O amine oxide aliphatic aromatic	 960± 20 1250± 50
N=O nitroso nitro	1550± 50 (str) 1530± 20 (as) & 1350± 30 (s)

Another FT-IR test was run by using a pure nitric acid as a standard sample to compare with the product from the experiment. Figure 3.5 show that the peak for both nitric acid product and standard sample has almost the same peak. Furthermore, both of the peaks are still in the range of nitro functional class which is 1500 -1700 cm^{-1}.

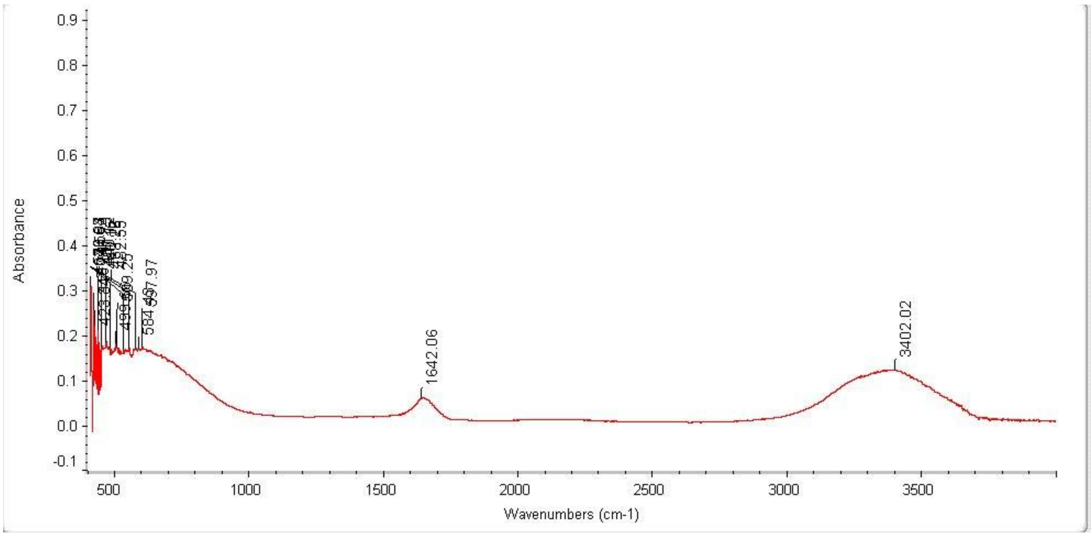

Figure 3.5: FT-IR of standard nitric acid

4. Conclusion

Based on the result in this research, it shows that the objective of this research is achieved. The main objective of this research is to recover NO_x recovered as nitric acid. Other objectives are to study the effect of conversion with presence of iron (III) oxide as catalyst as well as to study the effectiveness of photo-catalytic method.

At the beginning, the research did not progress as expected. However, after the research had been done, a lot of challenge had to be faced in order to achieve the objective of this study. Some of the problem is to install the 1000 watt metal halide lamp to the photo-reactor which needs a lot of adjustment and the reactor has to be calibrating again.

It could be concluded that this research is one of the solution to reduce the amount of oxides of nitrogen emitted to the atmosphere by reproducing them into nitric acid using photo-catalytic method. Furthermore, this method is economical and can be commercialize in many industries because they are highly demanded these days.

5. Recommendation

Based on the result and discussion, these recommendations can be taken into consideration to upgrade future studies of nitric acid production. First of all is to analyze the product by using Gas Chromatography – Mass Spectrometer (GC-MS) to give the more detail component of the product. Besides that, use more proper reactor which can withstand higher pressure. Moreover, using different type of catalyst such as titanium dioxide (TiO_2), activated carbon (AC) and ferric oxide (Fe_2O_3) will increase the quality of the research.

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