# STUDY OF HYDROGEN SULFIDE ($H_2S$) ADSORPTION BY USING COCONUT SHELL ACTIVATED CARBON

**SITI AMARLENA BINTI AHMAD**

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**by**

**SITI AMARLENA BINTI AHMAD**

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| | |
|---|---|
| AC | Activated carbon |
| BSU | Basic Structure Units |
| CSAC | Coconut shell activated carbon |
| IAC | Impregnated activated carbon |
| ID | Inner diameter |
| LPG | Liquefied petroleum gas |
| M | Molar (mol/L) |
| MFM | Mass flow meter |
| OD | Outer diameter |
| ppm | part per millions |
| PSA | Pressure swing adsorption |
| RH | Relative humidity |
| SEM | Scanning Electron Microscope |
| TEM | Transmission Electron Microscope |

# KAJIAN MENGENAI PENJERAPAN HIDROGEN SULFIDA MENGGUNAKAN TEMPERUNG KELAPA KARBON TERAKTIF

## ABSTRAK

Di Malaysia, tempurung kelapa adalah salah satu daripada bahan buangan pertanian yang utama. Skop utama kajian ini adalah untuk pengisitepuan karbonat kalium ke dalam karbon teraktif berasaskan tempurung kepala menggunakan kaedah pengisitepuan basah untuk meningkatkan kadar penjerapan dan meningkatkan penyingkiran $H_2S$. Komersial karbon teraktif yang telah diisitepuan dengan kalium karbonat dan digunakan untuk menjerap hidrogen sulfida ($H_2S$). Beberapa parameter yang dikaji dalam eksperimen ini adalah kepekatan kalium karbonat, masa pengisitepuan, suhu operasi, kepekatan $H_2S$ dan jumlah kadar aliran. Pengaruh parameter ini di atas kapasiti penjerapan boleh ditentukan. Karbon teraktif yang telah diisitepuan sebelum dan selepas penjerapan dianalisis menggunakan SEM. Keputusan eksperimen menunjukkan bahawa kepekatan kalium karbonat optimum dilonggokkan di atas AC adalah 1.0 M dan masa pengisitepuan terbaik ialah 2.0 jam. Apabila masa penumpuan dan pengisitepuan bertambah, kapasiti penjerapan meningkat sehingga menyebabkan karbonat kalium menyekat liang-liang dalam AC. Mekanisme penjerapan $H_2S$ oleh karbonat kalium berubat telah dicadangkan, yang fizikal penjerapan pada suhu operasi yang rendah dan penjerapan kimia pada suhu tinggi. Selain itu, garam alkali sebagai pengisitepuan menyebabkan AC cekap menjerap $H_2S$ pada kepekatan yang lebih rendah daripada $H_2S$. Pada kepekatan yang lebih tinggi $H_2S$, kapasiti penjerapan mengurangkan kerana semua liang roma yang penuh dengan sulfur sebagai produk tindak balas pengoksidaan.

# STUDY OF HYDROGEN SULFIDE ($H_2S$) ADSORPTION BY USING COCONUT SHELL ACTIVATED CARBON

## ABSTRACT

In Malaysia, coconut shell is one of the main agricultural wastes. The main scope of this study is to impregnate potassium carbonate onto coconut shell based activated carbon using wet impregnation method to increase the adsorption rate and enhance the removal of $H_2S$. The commercial activated carbons are impregnated with potassium carbonate and use it to adsorb hydrogen sulfide ($H_2S$). Several parameters studied in this experiment were potassium carbonate concentration, impregnations time, operating temperature, $H_2S$ concentration and total flow rate. The influences of these parameters on adsorption capacity can be determined. The impregnated activated carbon before and after adsorption was characterized using SEM. The experimental results revealed that the optimum potassium carbonate concentration deposited on AC is 1.0M and best impregnation time is 2.0 hour. As the concentration and impregnation time increase, the adsorption capacity increases until the potassium carbonates block the pores in AC. The adsorption mechanism of $H_2S$ by potassium carbonate impregnated was suggested, which is physical adsorption at low operating temperature and chemical adsorption at high temperature. Moreover, the alkaline salt-impregnated AC is efficient to adsorb $H_2S$ at lower concentration of $H_2S$. At higher concentration of $H_2S$, the adsorption capacity is reduce because all pores are filled with sulfur as the product of oxidation reaction.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Removal of Hydrogen sulfide ($H_2S$)

Hydrogen sulfide ($H_2S$) is a colourless gas with offensive odour. Its toxicity and odour has created a lot of environmental issue. Besides, this harmful gas may cause health problem. In industry, even the concentration is as low as 1 part per million (1ppm), hydrogen sulfide gas has detrimental effects on catalysts (Xiao et al., 2008b). Moreover, it can cause corrosion to equipments too. Hence, hydrogen sulfide must be removed from gases mixture to protect the environment, community and even the plant equipments.

There are various methods that can be used to treat hydrogen sulfide gas. For example, the gas is washing followed by neutralization with chemicals, adsorption onto activated carbon, condensation, masking, direct or catalytic combustion (Tsai et al., 2001) and pressure swing adsorption (PSA). PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species molecular characteristic and affinity for an adsorbent material. However, among these methods above, activated carbon adsorption is the most common and widely used method.

However, the $H_2S$ trace in the biogas, which is found to range between as low as about 50–10,000 ppm depending on the feed material composition to the digester, can cause corrosion to the engine and metal parts via emission of $SO_2$ from combustion, especially when the engine is not operated continuously, as well as toxic $H_2S/SO_2$

concentrations in the workplace. Therefore, $H_2S$ must be removed prior to further utilization. Common $H_2S$ removal technologies for $H_2S$ removal from biogas fall into one of the following: (1) absorption into a liquid either water or caustic solution; (2) adsorption on a solid such as iron oxide based materials, activated carbon or impregnated activated carbon and (3) biological conversion by which sulfur compounds are converted into elemental sulfur by sulfide oxidizing microorganisms with addition of air/oxygen (Horikawa et al., 2004, Pipatmanomai S. et al., 2009). Each technology has its own advantages and disadvantages.

These recovered biogas with its physical and chemical properties close to those of natural gas, albeit with a lower methane content, biogas can be used to boil water or for cooking instead of LPG, used as fuel for process heating, used for lighting purpose, produce electricity via internal combustion engine or used in replacement of diesel or gasoline to drive equipment.

## 1.2 Activated Carbon

Activated carbons are widely used for pollutants adsorption in gas phase and liquid phase. Variety of economy and industrial sector are using this material in the unit operation, such as chemical, petroleum, waste water treatment and automobile (Ioannidou and Zabaniotou, 2007). The activated carbon with high surface area can be produced from many source of carbonaceous material such as coconut shell (Vargas et al., 2011, Cagnon et al., 2009, Chiang et al., 2002), oil palm shell (Baroutian et al., 2010, Arami-Niya et al., 2012, Guo and Lua, 2003), olive stone (Juárez-Galán et al., 2009), rice husks (Yalçın and

Sevinç, 2000), wood (Srinivasakannan and Zailani Abu Bakar, 2004), peach stones (Soares Maia et al., 2010), cherry stones (Beker et al., 2010) and coffee residue (Boudrahem et al., 2009).

The coconut palm (*Cocos nucifera*) is a tropical palm tree that could be plant easily in Malaysia. The activated carbon that can be prepared from coconut shells, coconut husks and coconut coir had been proven by researchers which yield high surface area. Due to their high carbon content and hardness, coconut shells are an excellent raw material source to produce activated carbon. Activated carbons that are produced using coconut shells as the raw material are often sourced in geographic regions where coconuts are harvested, including India, Malaysia, Sri Lanka, and the Philippines.

All of the raw material had undergo carbonization process and activation process to achieve a high surface area and high pore volume to ensure great capability for the application of interest. Many factors in the carbonization process and activation process can be manipulated to obtain the ideal activated carbon. In the carbonization process or the pyrolysis, the factors of pyrolysis temperature affect significantly, followed by heating rate, the nitrogen flow rate and the residence time of pyrolysis (Ioannidou and Zabaniotou, 2007).

The carbonization process is the method to remove volatile matters from the carbonaceous material by thermal decomposition under inert atmosphere. The purpose of carbonization process is to produce the carbon structure and to create an initial porosity in the char under inert atmosphere. The temperature of carbonization process is between 600 to 700 °C and the products consist of fixed carbon called char.

Meanwhile, the activation process is the method to create the porosity of the AC. This activation process is very important because it determines the properties of AC and commonly there are two types of process of activation which are physical process and chemical process or both processes (physiochemical activation). The physical activation usually uses steam or $CO_2$ while the chemical activation usually uses $ZnCl_2$, $H_3PO_4$, KOH (Klijanienko et al., 2008) and etc.

### 1.3 Coconut in Malaysia

Coconut ranks fifth in Malaysia's agriculture in terms of cultivated area with oil palm and rubber occupying the greater portion. The coconut industry, however, still plays an important role in the country's economy providing livelihood to some 100,000 farm families or almost 10% of the nation's farming community.

In terms of area planted, the highest level was attained in 1982 at 363,000 hectares. Since 1986 at 330,000 hectares, the area planted to coconut was observed to be at a generally decreasing trend reaching to 315,000 hectares level in 1992 and down to 290,000 hectares in 1995.

Coconut in Malaysia is generally a smallholder's crop with 91% under smallholder cultivation and 9% under estate management. Of the total area planted to coconut, 63% is located in Peninsular, Malaysia, 19% in Sabah and 18% in Sarawak. With increasing labour shortage, decreasing productivity of palms and the massive conversion of coconut lands to oil palm plantation and other more profitable crops, the country projects a continuous decline in coconut area at a rate of 2.5-3.5% per year to some 285,000 hectares towards year 2000. It was estimated that about 32% of the total plantings are now well over 60 years old (Arancon, 1997).

The main constituents of a coconut, namely, meat, water, shell and husk are seldom all used and nearly always not at the same place. Over 90% of husks are wasted and in the case of shells it is 80% that are wasted. Only in India, Sri Lanka, Vietnam, Malaysia, and Thailand is the use of husks at a significant level. Roughly half of all coconuts produced are used for their meat being dried and expulsion of coconut oil. The second most important form of consumption is as fresh coconuts (RuralDevelopment, 2012a).

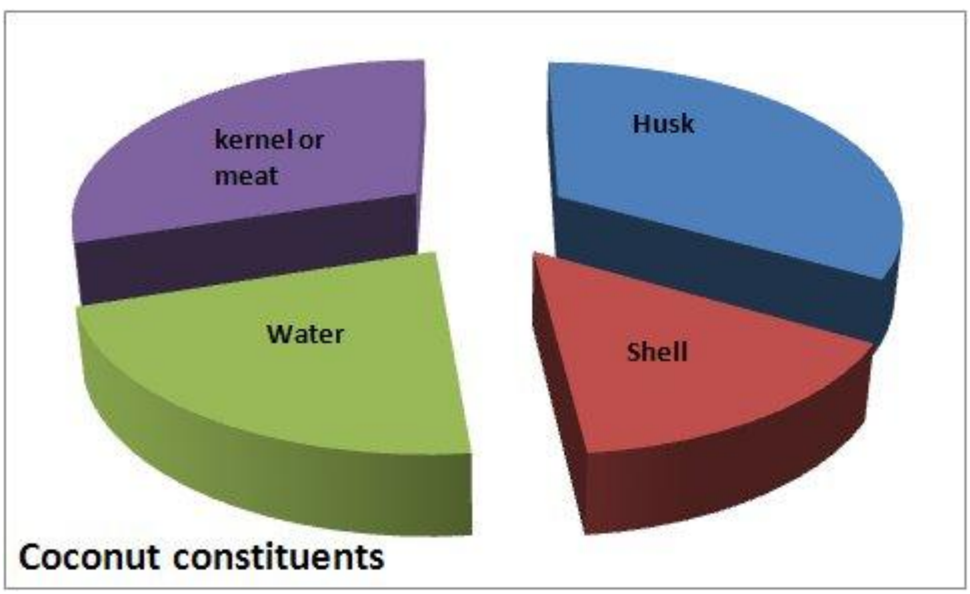


**Figure 1.1** The main constituents in coconut (RuralDevelopment, 2012b)

Roughly 15% of a coconut is made up of a hard shell, one of the hardest woods, and when transformed into charcoal, it is one-third the weight of the shells used. Burnt under conditions of controlled air supply, the shells become a charcoal, indeed an ideal one for barbecue purposes. Or it is used as raw material for production of activated carbon. In coconut producing countries shells are a valuable source of cooking fuel. In other countries the charcoal sells for premium prices.

Bulk use of coconut shell charcoal is mainly confined to activated carbon. Although coconut shell activated carbon is considered one of the finest carbons, prices have not been attractive due to a significant increase in production. Charcoal used to be and is still exported for activation but the process is also being undertaken in coconut producing countries like Philippines, Indonesia and Sri Lanka.

Coconut shell charcoal thus has an assured bulk price and a niche market high value. However, where activated carbon is produced, as it is in Philippines, Indonesia and Sri Lanka, it is a high value export product. Moreover, the market for activated carbon is growing at an accelerating rate due to increased demand for filtration devices that need it. Thus, at commercial market values - taking charcoal to have only its bulk value of $220 per ton, the following results:

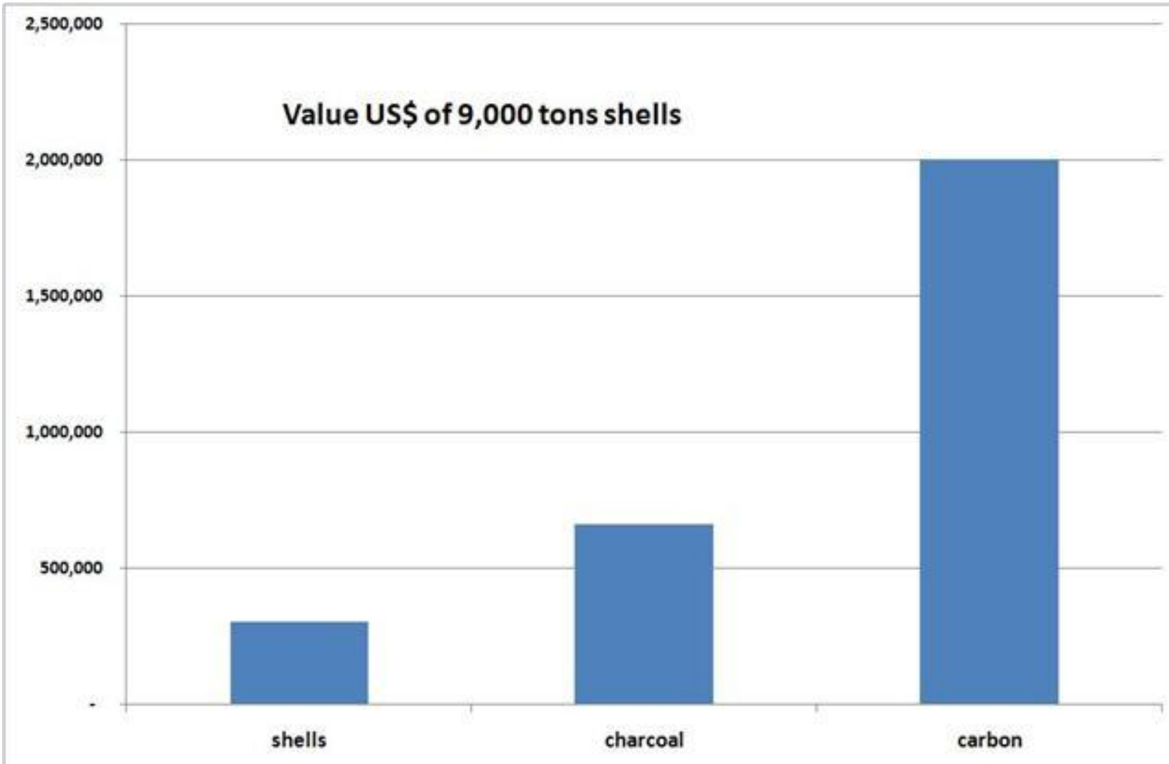


**Figure 1.2** Market values for coconuts' shells, charcoal and carbon (RuralDevelopment, 2012b)

## 1.4 Problem Statements

There are 2.4 billion coconuts every year in the Pacific Region (RuralDevelopment, 2012b). One of the ways to utilize the coconut shell waste is the waste can be use in the production of AC and the produced AC can be utilized in different ways to treat the air pollution. Furthermore, the world market for activated carbon in 2010 was estimated to be 1.2 million tons and the most mature market was on North America, Western Europe and Japan (Carbon, 2012). The increasing demand of the AC related to their unique properties and low production cost compared to other adsorbent that are available in the market. The AC is primarily used as adsorbent to remove pollutant from liquid, gas and organic compounds. Increase of environmental issues such as water and air pollution causes the increased need of AC. In this application AC produced is used in purification of poison gas from the gas streams, such as those used in water treatment and the processing of food, beverages and pharmaceuticals.

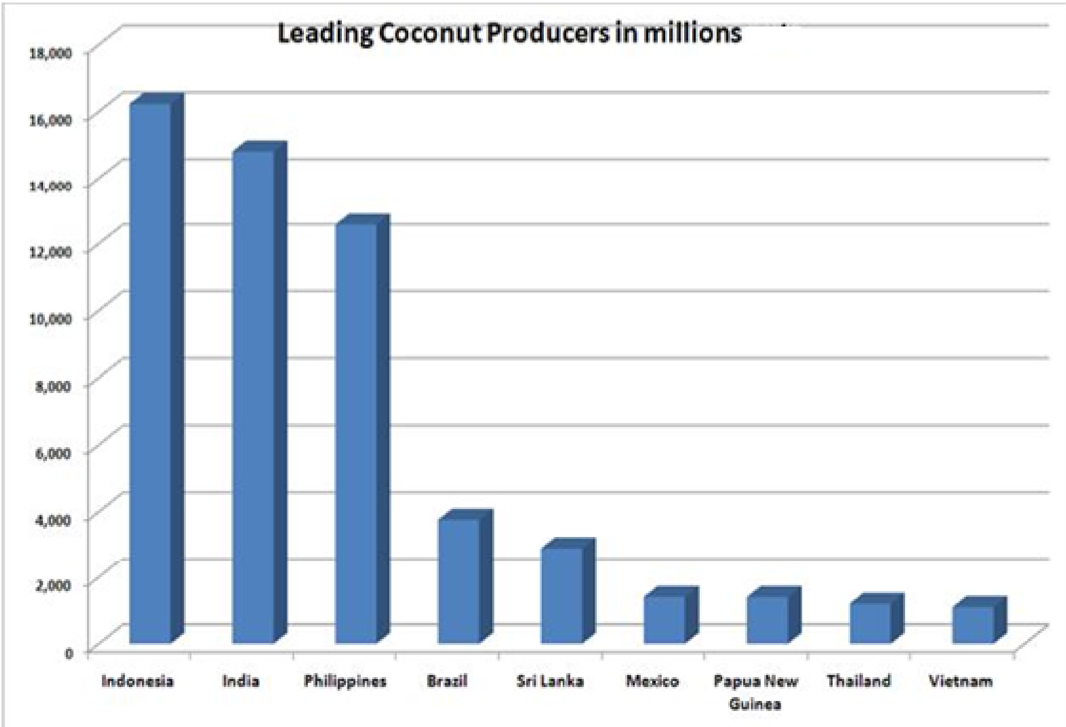


**Figure 1.3** Leading coconut producers in million (RuralDevelopment, 2012a)

Another problem is emission of hydrogen sulfide to the air. Hydrogen sulphide ($H_2S$), a ''rotten-egg'' smell gas produced from industrial processes, primarily from the extraction and refining of oil and natural gas and from paper and pulp manufacturing, but the gas is also present at sewage treatment plants, manure-handling plants, tanneries, and coke oven plants. It presents dual problems of its toxicity and foul odour. $H_2S$ can be detected by most people as low as 0.0047 ppm. Hydrogen sulfide emissions may pose a significant human health risk. One of the ways to utilize coconut waste is to produce activated carbon from coconut shell. Due to their high carbon content and hardness, coconut shells are an excellent raw material source to produce activated carbon. Their utilization in the activated carbon industries is a viable solution to this environmental issue. Besides, activated carbon from coconut shell is efficient to adsorb $H_2S$ gas as it has more microporous pore structure than coal-based AC. Based on previous study, impregnated AC give higher adsorption capacity than unmodified AC. Alkaline salt is been used as impregnation chemical because at least 2moles of $H_2S$ are adsorbed per one mole of $K_2CO_3$.

## 1.5 Research Objectives

The main purpose of this research is to study the effect of coconut shell activated carbon on hydrogen sulfide adsorption. The research was carried out according to the following objectives:

1. To study the effect of impregnation parameters such as potassium carbonate concentration and impregnation time on coconut shell activated carbon for adsorption of $H_2S$.
2. To determine the effect of $H_2S$ adsorption by using impregnated coconut shell activated carbon (CSAC) by varies adsorption temperature, $H_2S$ concentration and total flow rate of mixture gases ($H_2S$, $CH_4$ and $CO_2$) with calculating their adsorption capacity.
3. To characterized the impregnated coconut shell activated carbon for before and after $H_2S$ adsorption.

## 1.6 Scope of Study

As mentioned earlier, coconut shell has been reported as a promising biomass to produce AC which could be used for flue gas cleaning. Thus in this study, the preparation to impregnate CSAC by using potassium carbonate and its potential as a adsorbent to remove $H_2S$ was analyzed. Since there is many variables that affecting the adsorption of $H_2S$ on the activated carbon, however, this study focused only on the effect of five variables (potassium carbonate concentration, impregnation hour, adsorption temperature, $H_2S$ concentration and total flow rate of mixture gases).

Once the CSAC is prepared and impregnated it was analyzed for $H_2S$. Simulated flue gas containing $H_2S$, pure $CH_4$ and 99.9% of $CO_2$ with a total flow rate of 450ml/min was used to test the adsorption capacity of $H_2S$ on CSAC. Once the specified CSAC sorbent was obtained under optimum conditions (potassium carbonate concentration and impregnation hour) for maximum removal of $H_2S$ was found, a process study was done. This was done by varying the operating conditions of the adsorber i.e., feed concentration of $H_2S$ (ppm), operating adsorber temperature (°C) and total flow rate of mixture gases (ml/min).

The amount of $H_2S$ captured by CSAC sorbent was recorded continuously until it shows negligible activity/saturation (the outlet concentration of $H_2S$ becomes the same as the inlet concentration). After all the optimum conditions achieve, the CSAC will be send for characterized by using Scanning Electron Microscopy (SEM) to study the morphology of the CSAC.

## 1.7 Organization of Thesis

This dissertation consists 5 main chapters including chapter 1 to chapter 5. Each of the chapters provides information regarding the whole researches that have been conducted. Chapter 1 (Introduction) provides information regarding the basic outline of the whole thesis. It covers the introduction to coconut production in Asia Pacific region, the effect of hydrogen sulfide to human health and also the problems resulted from the coconut shell waste. This chapter also covers the problems statement and presents the current objectives of the research. Chapter 1 is ended with the organization of the dissertation.

Chapter 2 (Literature Review) is an extensive literature research. Literature research has been conducted especially on the areas that affecting most the main of the main task of the present research, the adsorption of hydrogen sulfide by using coconut shell activated carbon. The basic explanation regarding the properties and the production method of activated carbon and also the method used to remove hydrogen sulfide. Other information that related to the research is presented together with findings by others people.

Chapter 3 (Materials and Methods) describes the precursors and chemicals used throughout the research activity. After that, the method to impregnate coconut shell activated carbon by using potassium carbonate is present in this chapter. The experimental procedures for hydrogen sulfide adsorption on impregnated coconut shell activated carbon by using biogas scrubbing unit is presented well in this chapter.

Chapter 4 (Results and Discussion) is the core of this dissertation. This chapter presents the result obtained from the research and the optimized results based on sorption capacity were discussed. The effect of various operating conditions on sorption studies were conducted and analyzed. In the last section, it will discuss about the characterization for before and after the $H_2S$ adsorption.

Chapter 5 (Conclusions and Recommendations) concludes the overall results and discussions obtained from the previous chapter. In addition to that, some recommendations for future studies and improvement is suggested and well presented in this chapter.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Introduction

This chapter provides basic information on the adsorption of hydrogen sulfide ($H_2S$) by using coconut shell activated carbon. Basically, it covers the properties of hydrogen sulfide and the usage of coconut shell activated carbon to remove hydrogen sulfide.

## 2.2 Hydrogen Sulfide ($H_2S$)

Hydrogen sulfide ($H_2S$) is a colourless and flammable gas with the odor of rotten eggs. It is heavier than air with a specific gravity equal to 1.19. It can be produced naturally or by human industrial activities, especially associated with oil and gas industry (Swaddle, 1997). Hydrogen sulfide ($H_2S$) present in gas streams is considered as an environmentally hazardous material which can cause corrosion of equipment and catalyst poisoning (Craige and Anderson, 1995). In addition, this gas is a serious threat for personal safety (Ma et al., 2008). Hydrogen sulfide can remain in atmosphere for 15 hours and can be converted to sulfur dioxide ($SO_2$) and sulfuric acid ($H_2SO_4$) depending on process conditions. It is soluble in water and shows weak acidity function (ATSDR, 2012). Hydrogen sulfide is one of the significant causes of casualties in the gas industry (Dawe and Lucas, 2000).