

**REMOVAL OF SO₂ AND NO FROM FLUE GAS USING SORBENT
DERIVED FROM RICE HUSK ASH**

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**REMOVAL OF SO₂ AND NO FROM FLUE GAS USING SORBENT
DERIVED FROM RICE HUSK ASH**

by

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In the grace of the Lord Jesus Christ, and the love of God, and the fellowship of the Holy Spirit.

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LIST OF ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ANOVA	Analysis of Variance
BET	Brunauer-Emmett-Teller
CCD	Central Composite Design
DF	Degree of Freedom
DOE	Design of Experiment
EIA	Energy Information Administration
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
FGD	Flue Gas Desulfurization
F value	Fisher test value
MAQG	Malaysian Air Quality Guidelines
MOX	Malaysian Oxygen Berhad
NAAQS	National Ambient Air Quality Standards
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
Prob	Probability
RH	Rice husk
RHA	Rice husk ash
RSM	Response Surface Methodology
SCR	Selective Catalytic Reduction
SNCR	Selective non-Catalytic Reduction
SEM	Scanning Electron Microscopy
TLV	Threshold Limit Value

XRD	X-Ray Diffractometry
XRF	X-Ray Fluorescence
WHO	World Health Organization

LIST OF SYMBOLS

a	Activity
a_o	Initial activity
α	Rotatability of CCD
C_o	Inlet concentration of gas
C	Outlet concentration of gas
L	Sample coded for RHA _{inc} /CaO/NaOH/CuO sorbents
R	Sample coded for RHA _{raw} /CaO/NaOH/CuO sorbents
R^2	Correlation coefficient
x_1	Coded term of CuO loading
x_2	Coded term of RHA/CaO ratio
x_3	Coded term of hydration period
x_4	Coded term of NaOH concentration
y	Predicted sorbent sorption capacity
y_{SO_2}	Predicted sorbent sorption capacity of SO ₂
y_{NO}	Predicted sorbent sorption capacity of NO

**PENYINGKIRAN SO₂ DAN NO DARI GAS SEROMBONG
MENGUNAKAN BAHAN SERAP YANG DIHASILKAN DARIPADA ABU
SEKAM PADI**

ABSTRAK

Tujuan utama penyelidikan ini adalah untuk menghasilkan bahan serap daripada sekam padi bagi penyingkiran serentak SO₂ dan NO daripada gas serombong. Dalam penyelidikan ini, dua jenis abu sekam padi (RHA) digunakan iaitu RHA_{raw} dan RHA_{inc}. RHA dihidratkan dengan CaO dalam larutan NaOH dan seterusnya dicampurkan dengan CuO. Penyelidikan ini dijalankan dengan penyelidikan berstatistik ke atas parameter penyediaan bahan serap menggunakan perisian Design Expert. Parameter penyediaan bahan serap yang diselidik ialah jumlah CuO, nisbah RHA/CaO, masa penghidratan dan kepekatan NaOH. Keputusan menunjukkan bahawa jumlah CuO dan kepekatan NaOH adalah parameter penting yang mempengaruhi aktiviti bahan serap dalam penyingkiran SO₂ dan NO. Penyediaan bahan serap RHA_{raw} dan RHA_{inc} yang optimum ialah jumlah CuO sebanyak 3.06%, nisbah RHA_{raw}/CaO ialah 1.41, 8.05 jam masa penghidratan, kepekatan NaOH ialah 0.80M, dan jumlah CuO ialah 3.04%, nisbah RHA_{inc}/CaO ialah 1.41, 19.95 jam masa penghidratan, kepekatan NaOH ialah 0.20M, masing-masing. Selain itu, kesan parameter operasi seperti suhu, kepekatan awal SO₂ dan NO terhadap aktiviti penyingkiran SO₂ dan NO untuk bahan serap RHA_{raw} dan RHA_{inc} juga telah dikaji. Dua jenis pencapaian yang dikaji ialah penyerapan dengan 100% penyingkiran pencemar dicapai dan kecekapan penyingkiran pada keseimbangan. Lengkung bulus menunjukkan tindak balas di antara bahan serap dan

pencemar dipengaruhi oleh jenis RHA yang digunakan dalam menyediakan bahan serap. Secara umum, bahan serap RHA_{raw} mempunyai pencapaian yang lebih tinggi daripada bahan serap RHA_{inc} . Dalam penyelidikan ini, kapasiti serapan yang tertinggi untuk bahan serap RHA_{raw} dan RHA_{inc} masing-masing sebanyak 53.40mg SO_2/g bahan serap dan 6.90mg NO/g bahan serap; and 14.40mg SO_2/g bahan serap dan 4.95mg NO/g bahan serap.

REMOVAL OF SO₂ AND NO FROM FLUE GAS USING SORBENT DERIVED FROM RICE HUSK ASH

ABSTRACT

The main objective of this research is to synthesize a sorbent from rice husk for simultaneous removal of SO₂ and NO from flue gas. In this study, two types of rice husk ash (RHA), i.e. RHA_{raw} and RHA_{inc} were used. RHA was hydrated with CaO in NaOH solution and subsequently impregnated with CuO. The research was carried out by a statistical investigation on sorbent preparation parameters using Design Expert software. Investigated sorbent preparation parameters were CuO loading, RHA/CaO ratio, hydration period and NaOH concentration. The results showed that CuO loading and NaOH concentration are the major parameters that affect the sorbent's desulfurization and denitrification activity. The optimum sorbent preparation for RHA_{raw} and RHA_{inc} sorbents were 3.06% CuO loading, RHA_{raw}/CaO ratio of 1.41, 8.05 hours of hydration period, NaOH concentration of 0.80M and 3.04% CuO loading, RHA_{inc}/CaO ratio of 1.41, 19.95 hours of hydration period, NaOH concentration of 0.20M, respectively. In addition, the effect of operating parameters such as temperature, initial SO₂ and NO concentration towards RHA_{raw} and RHA_{inc} sorbents' desulfurization and denitrification activity were also studied. Two types of performances investigated were sorption at which 100% pollutants removal was sustained and equilibrium removal efficiency. The breakthrough curves showed that the reactions between sorbents and pollutants were affected differently, depending on which type of RHA used for sorbent preparation. In general, RHA_{raw} sorbent has higher performance than RHA_{inc} sorbent. In this study, highest sorption capacity at

100% pollutants removal for RHA_{raw} and RHA_{inc} sorbents were 53.40mg SO_2/g sorbent and 6.90mg NO/g sorbent; and 14.40mg SO_2/g sorbent and 4.95mg NO/g sorbent, respectively.

CHAPTER 1

INTRODUCTION

1.1 Energy Outlook

Energy has always been a crucial factor in our life. Ever since the industrialization era, energy consumption has been increasing significantly annually. Due to rapid economical development and population growth, the escalation of energy demand in the future could be foreseen. In Figure 1.1, the energy consumption from 1970 to 2020 is shown. From the projection of Energy Information Administration (EIA, 2001), energy consumption could reach 600 quadrillion Btu by year 2020. Therefore, energy supply is an important issue that concerns every nation and everyone.

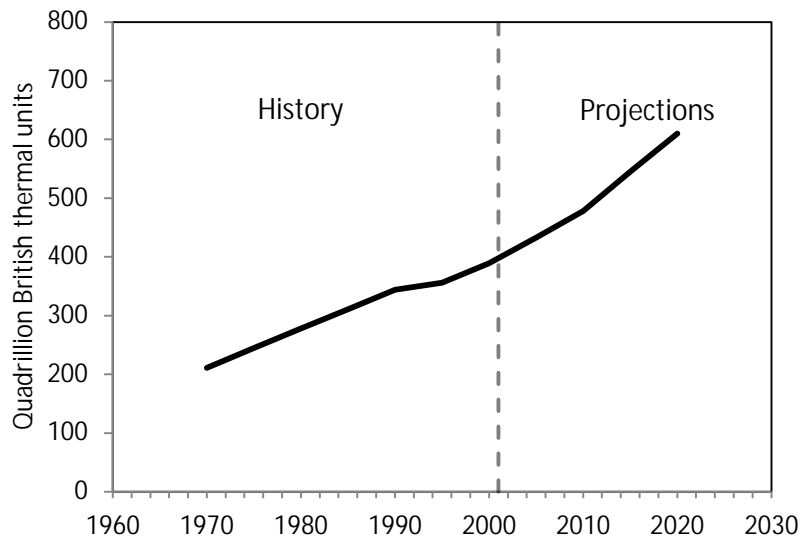


Figure 1.1. World energy consumption from 1970 until 2020 (EIA, 2001).

There are various forms of energy. However, the most commonly used form of energy are electricity and fuel. Electricity is generated through power plants by several methods such as generation of steam to spin turbine by fuel combustion and

renewable hydropower generation at dams. Further, fuel normally in liquid form such as petrol and diesel derived from crude oil is crucial for transportation purposes. Gaseous form of fuel such as natural gas is also utilized for special modified vehicles and cooking. There are many types of fuels that could supply energy for the purposes mentioned above.

Energy consumers could be divided into 5 sectors: power generation, industry, transportation, commerce and residential sector. For power generation, electricity is generated by combusting fossil fuel such as oil, gas and coal in order to generate steam to spin the turbine. In addition, nuclear power and renewable energy are other important sources of energy supply in power generation. A typical nuclear power plant could generate about 12.4 billion kWh and one of the world prominent user is USA in which it constitute 20% of the total energy supply mix (EIA, 2009a). However, nuclear power pose great danger towards the environment as possible radiation from leakage or explosion could cause lethal damage towards life form. Moreover, storage of nuclear waste is another factor to consider if construction of new nuclear power plant is being planned. Likewise, aligning with latest technological development, several types of renewable energies are available for power generation. Biofuel is one of the most important renewable energy that is growing fast as a source of energy along with hydropower and other type of renewable energies such as solar power and wind energy. The thought of renewable energy being an alternative is not forthcoming considering their uncertainty and instability in ensuring long term energy security. As for industry, other than electricity consumption for equipment, fuel combustion is important to supply energy/steam in the form of heat. Energy intensive industry such as iron and steel

industry, as well as petrochemical industry require large amount of fuel for their boilers in order to carry out their routine operations. Energy consumption from this sector is growing rapidly due to the immense economical development worldwide especially in China and India. For example, coal use in industrial sector is projected to grow 60% from 2006-2030 (IEA, 2009). Transportation sector utilize enormous amount of fuel (mainly liquid) as the amount of vehicles on road increases from year to year. For instance, transportation sector in the US consumed 28.8 quadrillion Btu in 2007 and the energy demand is expected to rise 0.4% annually to 31.9 quadrillion Btu in 2030 (EIA, 2009b). For commercial and residential sector, electricity is required for daily activities such as refrigeration, lighting, air conditioning, winter heating and utilization of various electrical appliances. In US, residential and commercial sectors' electricity consumption increased sharply over 1990-2008. From Figure 1.2, the electricity consumption had increased more than 50% in the time span to reach 1379 and 1352 billion kilowatt-hours, respectively for residential and commercial sectors. Nonetheless, based on the report from EIA, (2009b), the energy used for residential sector would only grow at 0.4% per year as a result of population growth, but largely offset by efficiency improvement in the lighting and electrical appliances. In this study, focus will be given to energy used for power generation.

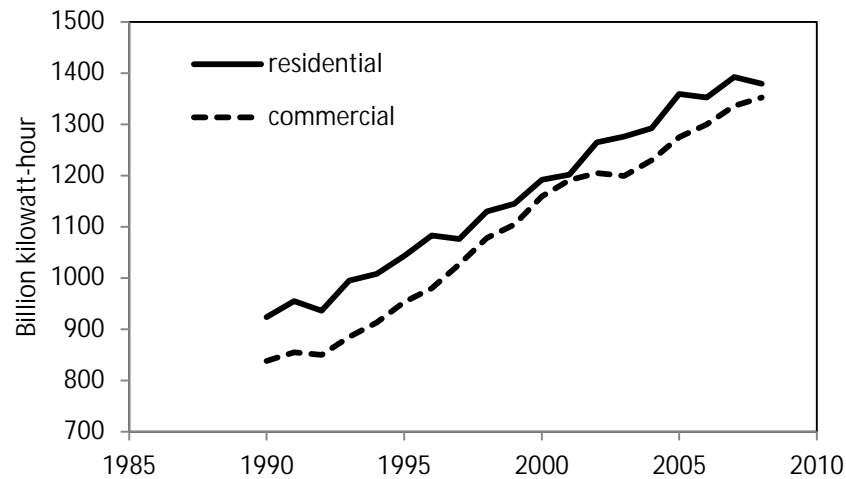


Figure 1.2. Electricity consumption of US for residential and commercial sectors (EIA, 2008a)

The energy supply mix for most of the world's nations consists of oil, gas, coal, nuclear and various types of renewable energy. By taking China as an example as shown in Figure 1.3, we could see that China does not rely on one type of energy source. Energy diversity is important to enhance energy security and avoid abrupt changes in energy supply which would cause devastation in economic development. Nevertheless, China relies on coal heavily as the energy supply by coal is as high as 62.80% of the total primary energy demand of the country (1,742 Mtoe). Moreover, other significant sources of energy in China are oil and biomass. However, the energy supply mix could vary from country to country depending on their nations' energy policy and resources availability. In Malaysia for instance, energy input to power generation in 2007 was 21910 ktoe. Natural gas was the largest energy source with 56.6% in comparison to coal with only 34.2% of the total energy supply in power generation. Apart from that, hydropower is a type of renewable energy that has contributed 6.9% (Malaysia Energy Database and Information System, 2007). Oil was not significantly used in power generation in Malaysia as it only consist 2.3%. Therefore, from the comparison of China and Malaysia, the energy supply mix

was rather different as their major energy source was coal and natural gas, respectively.

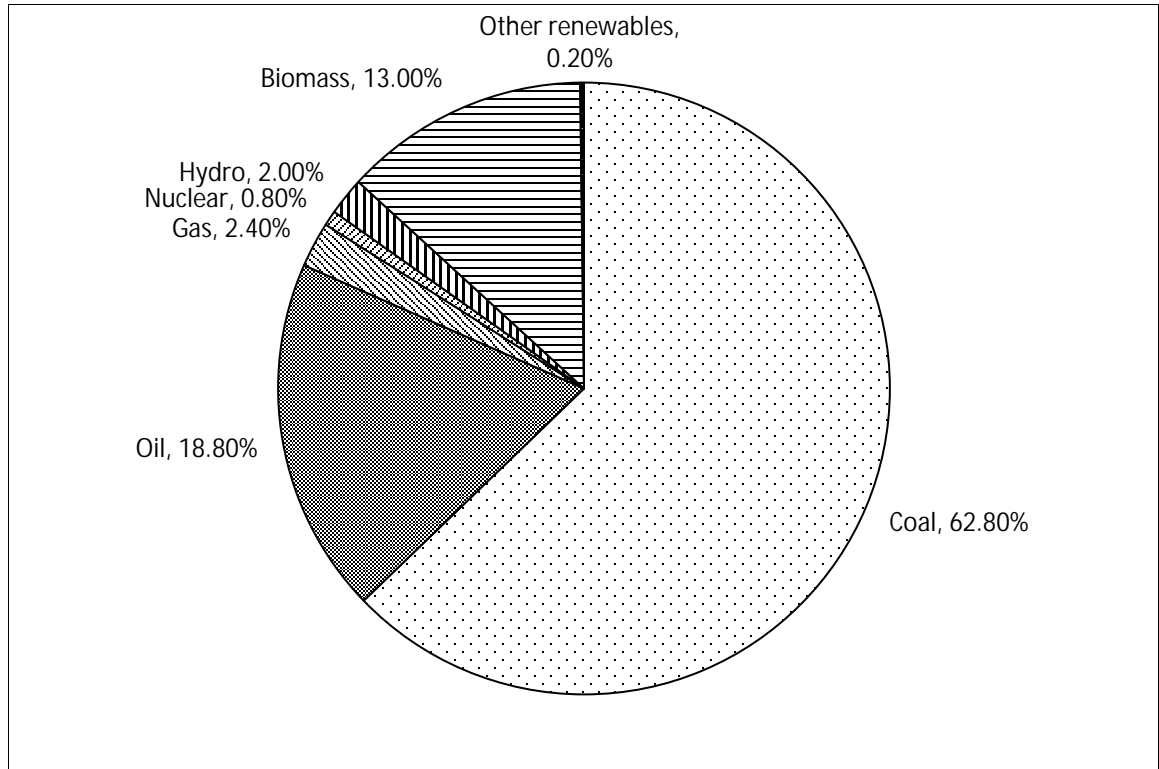


Figure 1.3. Primary energy demand in China, 2005 (IEA, 2007)

1.2 Importance of Coal as a Source of Energy for Power Generation

Fossil fuels such as oil, natural gas and coal are now the most important sources of energy used for power generation. Unfortunately, these fossil fuels are non-renewable and particularly for oil, its reserve is dropping very fast. According to a research by Society for Sedimentary Geology, proven petroleum reserve is about 1,000 billion barrels and would deplete in 36 years if the rate of utilization is maintained at current speed and no reserve is found (SEPM, 2008). Therefore, the necessity to find a substitution for oil is crucial for sustainable development in the future. Apart from the limited reserve, fluctuation of the price of crude oil is another

important factor that influences the role of oil as a source of energy. Price of crude oil could rise to unreasonably high and post huge pressure towards the economy of the world if the supply chain of oil is affected. Crude oil price could be affected by various factors from economical considerations to political instability. For example, the supply interruption due to Arab oil embargo towards countries that helped Israel in Yom Kippur war in 1973 had caused the price of crude oil to rise from \$3 to \$12 per barrel in 2008 dollar. Another oil price spike that occurred due to combination of Iranian revolution and subsequently Iraq-Iran war had caused crude oil price to increase from \$14 in 1978 to \$35 in 1981 (Williams, 2009). Therefore, in order to maintain stable economical development and avoid drastic changes in human living lifestyle, utilization of other energy sources is crucial.

There are other types of fossil fuels available other than oil, i.e, natural gas. Natural gas is mainly consists of methane and other hydrocarbons. It is normally found with petroleum deposit as the formation of both fuels is similar (Naturalgas.org, 2004). Natural gas is a relatively clean fuel as the combustion of natural gas releases very small amount of pollutants such as SO₂ and NO_x in comparison to oil and coal. Further, natural gas could be directly utilized as fuel after separation processes to remove impurities. Thus, there is a great potential for natural gas to substitute oil as the most important source of energy in the future. Nevertheless, from the work of Radler, (2008), world total natural gas reserves is 6,254 trillion cubic feet (Tcf). At current consumption rate of 103.5 Tcf annually, natural gas is expected to deplete in 60 years (EIA, 2008b). Therefore, although natural gas could replace petroleum after it depleted, natural gas itself would not last long because the consumption rate would boost and accelerate towards its depletion.

In a more recent development, renewable energies have been gaining attention worldwide recently in the quest of finding a substitute for petroleum. Renewable energies such as hydropower, solar, biomass, wind and geothermal will not deplete in time. Therefore, the shift in energy reliance from fossil fuels to renewable energies is the current trend of many governments' energy policy. Nonetheless, the percentage of renewable energies application is still low due to the price of renewable energies which are not economically competitive in comparison to fossil fuels. Much more technological development and researches are required before human could rely on renewable energy as the main source of energy supply.

Apparently, coal is the most abundant type of fossil fuel which could be found everywhere in the world. BP (2009) shows that coal is one of the most promising future sources of energy as proved reserve of coal is 826 trillion tonnes and it could last for another 122 years at current rate of consumption. As shown in Table 1.1, constitution of coal in the primary energy demand indicates that our society will heavily rely on coal in the projected future. However, combustion of coal could induce severe environmental problems such as acid rain and global warming. This is because although coal mainly consists of carbon but it also contains some sulfur and nitrogen compounds. During the combustion of coal in power plants, pollutants such as sulfur dioxide (SO₂) and nitrogen oxide (NO) could be emitted with the flue gas. SO₂ and NO gases are the primary causes of acid rain. A typical flue gas composition is shown in Table 1.2 (Toole-O'Neil, 1998; Granite, et al., 1999).

Table 1.1. Increase in world primary energy demand by fuel (IEA, 2007).

Energy demand increase (Mtoe)	1980-2005	2005-2030
Coal	1130	2130
Oil	870	1610
Gas	1130	1610
Nuclear	520	130
Hydro	130	175
Biomass	390	480
Other renewables	40	220

Table 1.2. Typical flue gas composition (Toole-O'Neil, 1998; Granite, et al., 1999).

Components	Concentrations
SO ₂	1000-2500ppm
NO	500-1000ppm
O ₂	4-10%
CO ₂	16%
H ₂ O	6%
Hydrocarbons	10ppm
Hg	1ppb
N ₂	Balance

1.3 Emission of Pollutants and Waste from Coal Combustion

Sulfur contained in the coal would react with oxygen from the air to form sulfur oxides (SO_x) during combustion. However, more than 90% of SO_x formed is SO₂ and its concentration in the flue gas could vary depending on the sulfur content in coal. Table 1.3 shows SO₂ emission limits for coal-fired power plants in some countries and recommended standards for SO₂ and NO made by some organizations. SO₂ emitted to atmosphere could form sulfuric acid droplets with water molecule in the air and subsequently drop to ground as acid rain. Likewise, combustion of coal could produce NO from either fuel or air. Although NO concentration in flue gas is

normally not more than 500ppm, acid rain could still form as NO dissolve in water molecule to produce nitric acid. The acid rain formed either from SO₂ or NO with pH range from 3-5 would destroy plantation and aquatic life. In addition, acid rain would also corrode building and cause huge monetary lost. With the prediction of more coal-fired power plants operating in the future, the effort in Kyoto Protocol is nullified. Furthermore, NO is one of the precursors that would undergo photochemical reaction with volatile organic compounds (VOCs) and sunlight to form tropospheric ozone (O₃). Tropospheric ozone is a reactive oxidant gas that causes atmospheric smog. Exposure to tropospheric ozone could cause health problem especially on the respiratory system (World Bank Group, 1998).

Therefore, predicaments of balancing economical development and environmental considerations are inevitable as massive emission of SO₂ and NO from coal combustion could not be avoided in order to reduce the cost of power; simultaneously enhance the magnitude of acid rain, global warming and environmental pollutions. Currently, SO₂ and NO control technologies are carried out in multi stage operation. Desulfurization is mainly carried out through flue gas desulfurization (FGD) technology by spraying slurry calcium compounds (sorbents) such as calcium hydroxide (Ca(OH)₂) and calcium oxide (CaO) in the flue gas stream. SO₂ in the flue gas stream will react with calcium in the slurry to form sludge that mainly contains CaSO₄. In this wet type FGD, large amount of corrosive sludge is generated and therefore requires slurry handling facilities that is very messy. Furthermore, conversion of calcium compounds is generally very low due to low surface area of the sorbent used. Apparently, for denitrification process (NO removal), selective catalytic reduction (SCR) is the more popular choice using

catalyst-support type sorbent. Some of the common sorbents under research are Cu-Mn-CeO_x/Al₂O₃/Al Alumite catalyst (Guo et al., 2004) and zirconia-supported cobalt catalyst (Tsyntsarski et al., 2003). Further, some catalysts with activated carbon as support are also investigated by Zhu et al. (1999) and Zhu et al. (2000). In these studies, copper oxide and vanadium oxide were used as active components to reduce NO by NH₃.

Table 1.3. Various threshold limits for SO₂ and NO.

Pollutants	Countries/organizations	Coal-fired power plant limits (ppm)¹	Standards (air quality/ambient) (ppm)
SO ₂	Malaysia	350	n.a.
	USA	260	n.a.
	Australia	70	n.a.
	Germany	140	0.021 (annual average) ²
	Japan	50-200 (plant specific)	n.a.
	Belgium	400	
	MAQG ³		0.037 (24h average)
	WHO ⁴		0.007 (24h average)
			0.175 (10min)
	NAAQS ⁵		0.028 (annual average)
		0.128 (24h average)	
	ACGIH-TLV ⁶		2
	OSHA-PEL ⁶		5
NO	ACGIH-TLV ⁶		25
	OSHA-PEL ⁶		25

¹Yugeta (2001); ²Kiely (1997); ³Afroz et al. (2003); ⁴WHO (2006); ⁵de Nevers (2000); ⁶OSHA/EPA Occupational Chemical Database, (2007).

MAQG (Malaysian Air Quality Guidelines); WHO (World Health Organization); NAAQS (National Ambient Air Quality Guidelines); ACGIH-TLV (American Conference of Governmental Industrial Hygienists-Threshold Limit Value); OSHA-PEL (Occupational Safety and Health Administration-Permissible Exposure Limit)

Apart from the emission of pollutants, combustion process also leaves behind a huge quantity of ash. For instance, combustion of rice husk will leave behind rice husk ash (RHA). Since Malaysia has a very big rice industry, the ash or also known as siliceous material is fast becoming a threat to environment due to massive amount of waste produced. From Table 1.4, world paddy productions had been increasing over year 2005-2008. The amount of paddy produced rose from 632 million tonnes to approximately 685 million tonnes in accordance with the increase of world population as paddy is the main food for many countries especially those in Asia. After paddy is processed in rice milling factory, there is a necessity to handle a large amount of rice husk which is about 20% of the paddy production. Rice husk is normally combusted for heat generation as it contains heat energy of 16,720 kJ/kg (Della et al., 2002). Else, rice husk is discarded to cause not only material waste but environmental pollution as well. As for the production of rice husk ash as shown in Table 1.4, approximately 24.6 million tonnes of RHA was produced in 2008 and this amount is increasing annually. The content of RHA is mainly amorphous silica (92-95%) and other metallic impurities (Bronzeoak, 2003). RHA has been considered as an important source in the production of silicon compounds (Andreoli et al., 2000), fertilizer for plantation, and in the preparation of concrete and cements (Della et al., 2002). Nevertheless, RHA is not fully utilized as it is mostly dumped and causes environmental pollution.

Table 1.4. Paddy productions from 2005 – 2007 (FAO Statistics Division, 2009).

Productions (tonnes)	2005	2006	2007	2008
World paddy	632,271,515	641,636,358	659,590,623	685,013,374
Malaysia paddy	2,314,000	2,187,000	2,375,000	2,384,000
World rice husk ¹	126,454,303	128,327,272	131,918,125	137,002,675
World rice husk ash (RHA) ²	22,761,775	23,098,909	23,745,263	24,660,481

Estimation (Bronzeoak, 2003): ¹Rice husk = 20% paddy production, ²RHA=18% Rice husk.

1.4 Problem Statement

Coal could be one of the most significant sources of energy in the future as oil and gas reserves are depleting fast. The major pollutants from coal combustion are SO₂ and NO, which are the precursor of acid rain. Current available abatement technology is expensive as it involves sorbent preparation from expensive materials such as rare metals. Therefore, research on cheaper sorbent is critical in order to achieve cost reduction in abatement technology. Hence, this research intends to utilize cheaper metal and natural waste in the sorbent synthesis to remove pollutants from flue gas, simultaneously achieving the objectives of environment protection and retaining sustainable development.

1.5 Research Objectives

The main objective of this research is to synthesize sorbents from different type of rice husk ash in order to be utilized in the simultaneous SO₂ and NO removal technology. There are several measurable objectives of this study and are listed as follows.

1. To determine the effect of several sorbent preparation parameters towards sorbent's desulfurization and denitrification performance by using statistical design of experiments.
2. To optimize of sorbent preparation parameters in order to synthesize sorbent with highest performance.
3. To observe the effect of operating conditions towards sorbent's desulfurization and denitrification performance.

1.6 Thesis Layout

There are five chapters in this thesis. Chapter 1 (Introduction) highlights the energy outlook of several countries such as the US, China and Malaysia. Further, a brief discussion on utilization of coal as a source of energy for power generation was also included in this section. Subsequently, an overview of the pollution caused by pollutants from coal combustion was described and available abatement technology is listed. In addition, problem of RHA accumulation was also being discussed followed by the problem statement that explains the necessity of this project. In the last section of this chapter, thesis layout was given in order to summarize the content of this thesis.

Chapter 2 (Literature Review) elaborates some SO₂ and NO control technologies. Simultaneous removal of SO₂ and NO technology was also included with applications of RH/RHA and copper sorbent. Besides that, some basic background of the experimental design and methods that were relevant to this research are also given in this chapter.

Chapter 3 (Materials and Methods) lists all the materials and chemicals used in this study. Following section describes the sorbent preparation methods and statistical experimental design. Details of experimental set-up for the sorbent sorption studies were also presented with characterization procedures included in the last section.

Subsequently, Chapter 4 (Results and Discussion) as the core part of this thesis is divided into 5 sections. First two sections depict the effect of sorbent preparation parameters such as copper loading, hydration period, RHA/CaO ratio and NaOH concentration towards desulfurization and denitrification activity of sorbents derived from RHA_{raw} (untreated dark gray rice husk ash) and RHA_{inc} (white rice husk ash obtained from rice husk acid leaching and follow by incineration) by using experimentation tool (Design Expert). XRD and SEM were carried out for selected sorbents in order to identify the species that involves in the reaction. In addition, optimization of sorbents derived from RHA_{raw} and RHA_{inc} were also conducted in order to synthesize sorbents for following sections. In the third and forth section, the effect of operating parameters such as temperature, concentration of SO₂ and NO towards desulfurization and denitrification activity of sorbents derived from RHA_{raw} and RHA_{inc} were also discussed based on breakthrough curves. In the last section, comparison between sorbents derived in this study and various sorbents reported in literature were discussed.

Chapter 5 (Conclusions and Recommendations) gives conclusions of the findings obtained and recommendations for future research related in this field.

CHAPTER 2

LITERATURE REVIEW

This chapter summarizes some information on various types of sorbents and materials that are currently being used in the research to control SO₂ and NO. In addition, sorbents developed for simultaneous removal of SO₂ and NO will be given special focus. Moreover, research on the applications of rice husk (RH), rice husk ash (RHA) and copper sorbent for various purposes are also presented. Finally, the experimental design and method used in this research are also included.

2.1 Research on SO₂ Removal

Stringent regulations and laws were enacted by governments all over the world to assure environmental protection by setting a limit for SO₂ emission as shown in previous Table 1.3. In order to control SO₂ emission, flue gas desulfurization (FGD) technology had been utilized to reduce SO₂ from flue gas. Currently, wet type FGD is more commonly used in industry utilizing calcium based sorbents such as lime and limestone in slurry. Nevertheless, this type of operation involves the handling of large amount of slurry and sludge. Thus, it requires extra investment for materials handling and new/special equipment in order to achieve environmental protection, subsequently increase the cost of the overall process. Therefore, research interests in reducing cost of FGD especially in dry type FGD had been widely investigated in the last decade. In dry type FGD, sorbent is injected directly in the duct to react with flue gas. Due to the short residence time, sorbent used should be highly reactive and possess high sorption capacity towards SO₂. Currently, for most researchers, calcium based sorbents are of high interest. Calcium

compounds such calcium hydroxide (Ca(OH)_2), calcium carbonate (CaCO_3), calcium sulfate (CaSO_4) and calcium oxide (CaO) were added to inert supports derived from ash, i.e. rice husk ash, coal fly ash, oil palm ash in order to increase the surface area of the sorbent. Increased sorbent surface area would then improve sorption rate and capacity, and this is important to ensure the technical and economical viability of the sorbent.

Lee et al. (2005b) investigated SO_2 removal activity by sorbent derived from $\text{CaSO}_4/\text{CaO}/\text{fly ash}$. Sorbent preparation parameters such as amount of starting materials (CaSO_4 , CaO and fly ash) and hydration period were correlated with sorbent surface area by using Design Expert software. $\text{CaSO}_4/\text{CaO}/\text{fly ash}$ sorbents were found to have surface area ranging from 22.5-133.33 m^2/g . In their study, desulfurization activity of these sorbents (in $\text{mg SO}_2/\text{g CaO}$) was correlated well with their surface areas with a correlation coefficient value of 0.991. By subjecting simulated flue gas containing 1000ppm SO_2 , 500ppm NO , 5% O_2 , 12% CO_2 and balance N_2 at 150°C , desulfurization performance of $\text{CaSO}_4/\text{CaO}/\text{fly ash}$ sorbent was compared with the starting materials. The results showed that desulfurization activities for the derived sorbents were found to be significantly higher in comparison to the starting materials. They also concluded that the sorbent surface area ($64.5\text{m}^2/\text{g}$) was much higher than the starting materials ($1.5\text{-}5.6\text{m}^2/\text{g}$) and these contributed to the higher desulfurization activity. In addition, the effect of temperature and NO concentration towards sorbent desulfurization performance were also studied. Increasing temperature from $60\text{-}200^\circ\text{C}$ was found to favor desulfurization activity but further temperature increase did not show significant changes. As for effect of NO concentration, the study showed that presence of NO

avored desulfurization activity. This is because NO_2 formed from NO could oxidize SO_2 to SO_3 that is more reactive towards calcium compounds in the sorbent.

Apart from coal fly ash, Zainudin et al. (2005) used oil palm ash (OPA) as siliceous material for hydration process with calcium compounds (CaO , CaSO_4 , $\text{Ca}(\text{OH})_2$). In their work, sorbent with highest surface area was found to be $134.2\text{m}^2/\text{g}$ and the most significant sorbent preparation parameter that affects the surface area of derived sorbent was hydration period. Increasing hydration period for hydration process could produce sorbent with higher surface area. Contrary to hydration period that has significant effect towards sorbent surface area, amount of CaSO_4 was found to have no significant effect. CaSO_4 was found to suppress the crystal growth of $\text{Ca}(\text{OH})_2$ during hydration process for coal fly ash but not for oil palm ash. Therefore, addition of CaSO_4 did not affect the sorbent surface area. Desulfurization activity study was carried out by Zainudin et al. (2005) using a feed gas stream of 500-2000ppm SO_2 , 5% O_2 , 12% CO_2 , 30% humidity and balance N_2 at operating temperature of 100°C and showed that desulfurization activity dropped with increasing SO_2 concentration. Further, sorbent with $\text{Ca}(\text{OH})_2$ addition during hydration period has higher desulfurization activity in comparison to sorbent synthesized with CaO .

In addition, application of rice husk ash (RHA) as a source of siliceous material with CaO/CaSO_4 in desulfurization activity was also investigated (Lee et al., 2005a). Hydration temperature and amount of RHA were found to be important in the preparation of sorbent with high surface area. Nevertheless, the study showed that interaction between hydration period and amount of RHA was more significant

than other first order terms. Therefore, in order to synthesize sorbent with high surface area, interaction effect of hydration period and amount of RHA should be given utmost attention. Desulfurization study of the sorbents derived from RHA/CaO/CaSO₄ showed that sorbent with higher surface area has higher utilization of Ca²⁺ and is in accordance with higher desulfurization sorption capacity. Further analysis with sorbent prepared from RHA and CaO done by Dahlan et al. (2006) revealed that temperature and amount of water in hydration process were insignificant towards sorbent's desulfurization performance. Significant parameters found in this study were hydration period, amount of RHA and CaO that have similar level of significance towards sorbent desulfurization performance. By subjecting sorbent to simulated flue gas of 2000ppm SO₂, 500ppm NO, 10% O₂ and balance N₂ at operating temperature of 100°C, 100% SO₂ removal achieved after 20min at optimum condition (16h hydration, 15g RHA, 4g CaO, 100mL H₂O and 200°C hydration temperature). In subsequent research done by Dahlan et al. (2009), desulfurization activity of RHA/CaO sorbent was found to increase with additive such as NaOH and K₂HPO₄ in the hydration process. The explanation made by Dahlan et al. (2009) was that existence of additive has promoted the dissolution rate of silica from RHA. Ultimately, formation of Si-Ca complex that has high SO₂ sorption activity was increased.

2.2 Research on NO Removal

Both regulation and recommended NO concentration in ambient air by ACGIH-TLV (American Conference of Governmental Industrial Hygienists-Threshold Limit Value) and OSHA-PEL (Occupational Safety and Health Administration-Permissible Exposure Limit) is 25ppm as NO is a harmful pollutant

(OSHA/EPA Occupational Chemical Database, 2007). In addition, increased emission of NO has also raised governmental effort to reduce their emissions to protect the environment. This is mainly due to the characteristic of NO that is capable of causing acid rain. Therefore, abatement of NO emission is crucial. Currently, research trend in reducing NO emission is concentrated on post combustion process instead of removing nitrogen compound from the fuel. NO reduction can be mainly categorized as selective catalytic reduction (SCR) and selective non catalytic reduction (SNCR). SCR involves application of supported catalysts which could accelerate reduction process between NO molecules and reducing agent such as ammonia (Huang et al., 2003). Most of these catalysts are metal oxide supported on inert materials to give material strength and improved surface area for better catalytic activity. Metal oxides such as vanadium oxide (V_2O_5) (Zhu et al., 2001; Huang et al., 2003), platinum (Pt) (Kikuyama et al., 2002), zirconia (ZrO_2) (Kikuyama et al., 2002), copper (Cu) (Byeon et al., 2008), manganese (Mn) (Chen et al., 2009), and cerium oxide (CeO) (Chen et al., 2009) were utilized as the active components in catalytic reaction with NO molecules. Further, some of inert materials utilized were zeolite (Chen et al., 2009), alumina (Kikuyama et al., 2002), silica and activated carbons (Zhu et al., 2001; Park & Kim, 2005; Byeon et al., 2008; Huang et al., 2003). However, there are some limitations of these sorbents in denitrification activity. Existence of other component in flue gas such as SO_2 can deactivate the sorbent due to the formation of sulfates from the reactions of SO_2 and metal oxides.

In two independent works, Zhu et al. (2001) and subsequently Huang et al. (2003) had investigated the feasibility of vanadium oxide (V_2O_5) supported by

activated carbon (AC) to reduce NO. The activated carbon used in this research was prepared from commercial coal-derived semicoke which undergone several steps of activation and oxidation process before impregnated with aqueous solution of ammonium metavanadate in oxalic acid. By using ammonia (500-600ppm) as the reducing agent and initial 500ppm of NO in the feed stream, steady state NO conversion reached at 92.2%. Besides, steady state conversion could be improved to 97.3% if tin oxide (SnO_2) was used. Nevertheless, performance of this catalyst was affected by addition of SO_2 and H_2O in the feed stream. These molecules had caused deposition of ammonium sulfate on the catalyst surface and subsequently causing pore plugging and surface area losses. In addition, since 100% reduction of NO could not be achieved, this indicates that emission of NO is still inevitable particularly at lower NO concentration.

Kikuyama et al. (2002) investigated the Pt-ZrO₂/Al₂O₃ catalyst and showed good denitrification activity as 100% removal of NO was achievable. In their study, 800ppm of NO in feed stream was flowed through catalyst with weight of catalyst to flow rate of feed ratio (W/F) of 1.0 g.s.cm⁻³. This system could sustain 60 minutes of 100% NO removal but it was not economically feasible as amount of catalyst required for a prolonged denitrification activity was enormous. In another research done by Chang et al. (2009a) showed good denitrification activity as 60 minutes of 100% NO removal was achieved at higher flow rate (600mL/min) but using only 0.5g catalyst. In this study, catalyst used was derived from rhodium (Rh) supported by alumina (Al₂O₃). The catalyst was prepared using impregnation method by adding aqueous rhodium solution to Al₂O₃ support. Nevertheless, the derived catalyst was used to reduce NO from municipal solid waste incinerators (MSWIs) which contain

relatively lower NO concentration (200ppm) if compare to NO concentration in flue gas from coal combustion. Apart from that, flue gas from MSWIs contains hydrogen chloride (HCl) which does not appear in flue gas from coal combustion.

Activated carbon fiber (ACF) was also used as support in the research done by Park & Kim (2005) and Byeon et al. (2008). Silver (Ag) nanoparticles were deposited on ACF by electroplating (Park & Kim, 2005). Ag/ACF was able to achieve 100% removal of NO for 45 min at 10mL/min of 1000ppm NO stream. Besides, copper addition by electroless deposition on ACF done by Byeon et al. (2008) was effective to remove NO in low concentration (160 ppm). By utilizing 3g of Cu/ACF sorbent and flow rate of 3L/min, approximately 20 minutes was sustained for 100% NO removal at optimum condition. In addition, study on the effect of temperature towards denitrification activity showed that optimum sorption activity occurred at approximately 150°C.

Other than activated carbon, zeolite emerges as a good source of adsorbent which has good surface area and structure as a support for active species. Chen et al. (2009) made use of transitional metal oxides/zeolite to purify CO₂ stream by adsorption. Fe, Co, Ni, Mn, Co and Ce oxides were added to zeolite (HZSM-5) by incipient wetness impregnation method. Resulting sorbents were applied in the denitrification study of 110-118.3mL/min feed stream containing 150-200ppm NO at 20°C. By analyzing the results, Cu/HZSM-5 was found to have good NO sorption capacity in the feed stream containing CO₂ (4.06mg/g) and O₂ (16.42mg/g). Further, other sorbents such as Co/HZSM-5 and Ni/HZSM-5 also showed comparable NO sorption capacity.

Apart from SCR, SNCR make use of reducing agent in NO reduction process and do not involve application of catalyst. In the work of Bae et al. (2006), NO reduction with NH_3 and various types of additives was analyzed. Three types of additives were gas additives (CO , CH_4), alcohol additives (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$) and volatile organic compounds ($\text{C}_6\text{H}_5\text{OH}$, C_7H_8). The experiments were carried in such a way that 300 ppm NO stream with particular additives and NH_3 was flowed at 47L/min through a reactor packed with α -alumina particles (3mm) as packing media to improve gas mixing. Moreover, reaction temperature was set between 973-1323K. The findings showed that these additives improve the optimum reaction temperature and removal efficiency by some extent depending on type of additive and normalized stoichiometric ratio ($\text{NSR} = [\text{additive}]/[\text{NO}]$) used. Nevertheless, in this study, highest NO removal efficiency achieved was about 75% only, probably due to low residence time (1.4s). Therefore, SNCR is a less suitable method for denitrification of flue gas from coal combustion. High reaction temperature contributes to inadequacy in this method because heat integration is normally applied in order to recover the heat contained in the flue gas, directly improving combustion efficiency of fuel.

2.3 Research on Simultaneous Removal of SO_2 and NO

Multi stage removal of pollutants from flue gas is very expensive due to high capital cost and operating cost. To make matter worse, stringent pollutants emission limit has been imposed on flue gas worldwide by policy makers to protect the environment. Therefore, power supply sector in many countries particularly developing countries are finding it hard to meet the emission limit due to limited findings on abatement technologies. In order to overcome this problem, simultaneous

removal of SO₂ and NO from flue gas can be a potential and crucial solution to reduce the capital and operating cost of air pollutants control technology, making it more economically feasible. Recent research showed that many materials could be utilized in the objective of removing SO₂ and NO simultaneously in single stage operation. Materials such as metals oxides, activated carbons and ashes could act as active components and supports for simultaneous desulfurization and denitrification activity.

Vanadium oxide (V₂O₅) has been a popular compound used in many researches for various purposes. Utilization of V₂O₅ supported with activated carbon was carried out by Ma et al. (2008) and Guo et al. (2007). In the work of Ma et al. (2008), simulated flue gas stream with 500ppm NO and 1500ppm SO₂ at space velocity of 6450L/kg.h flowing through V₂O₅/AC catalyst. At optimum condition of 200°C and 9% vanadium loading, SO₂ sorption capacity for 100% removal efficiency was 119.8mg/g. However, NO removal efficiency was only 60% instead of achieving 100% as in desulfurization activity. Nevertheless, research of Guo et al. (2007) indicated that modification on V₂O₅/AC catalyst could be done by NH₃ regeneration in order to achieve 100% removal of NO. Guo et al. (2007) investigated the feasibility in SO₂-captured catalyst regeneration for the simultaneous removal of SO₂ and NO. In this study, spent catalyst from desulfurization activity undergoes regeneration at 200-380°C, 0-5% NH₃ and regeneration time of 10-80min. It was found that at optimum regeneration condition, regenerated catalyst could achieve original SO₂ sorption capacity and notably, removal efficiency for NO improved from 55% to 100% and sustained for about 13min at the operating condition of 200°C, space velocity of 7800h⁻¹, 0.15% SO₂, 0.05% NO and 0.05% NH₃.

Availability of NH_3 in the regeneration process modified the catalyst surface and allows deposition of NH_3 in the form of NH_4^+ on the catalyst, which subsequently increase NO removal efficiency. Therefore, introduction of NH_3 in the sorbent preparation could help in surface modification and improves the sorbent sorption capacity.

Activated carbon is another type of sorbents currently under research for removal of pollutants from flue gas in a single stage process. Davini (2002) showed that activated carbon prepared from oil-fired fly ash was successful in achieving this objective. Solid particle from the combustion of heavy oils (oil-fired fly ash) could be treated by HCl and HF solution followed by activation by CO_2 . Subsequently, resulted activated carbon was tested for desulfurization and denitrification activity by synthetic flue gas containing 1000ppm SO_2 and 500ppm NO. The result indicated that performance of prepared AC was highest at low temperature and decreased with increasing temperature. The saturated sorption capacity for AC after the system operated for 3 hours at flow rate of 3L/hr was 85mg SO_2 /g sorbent and 45mg NO/g sorbent. AC from oil-fired fly ash showed good activity in the removal of pollutants because it has high surface area of $1000\text{m}^2/\text{g}$. Unfortunately, Davini (2002) did not report whether 100% removal efficiency was achieved.

Recently, a relatively new method called microwave technology has been developed. One of the applications in environmental protection is as shown in the work of Wei et al. (2009). In their research, simultaneous desulfurization and denitrification study was carried out by microwave reactor with ammonium bicarbonate and zeolite as the catalyst and support. Even though catalyst preparation