REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING RICE HUSK ASH/CaO/CeO_2 SORBENT

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REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING RICE HUSK ASH/CaO/CeO_2 SORBENT

by

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This Thesis is dedicated to my beloved
Father (Hj. Dahlan Mansyoer), Mother (Hjh. Rasuna Harun),
Wife (Nurbaiti), Kids (Syifa & Najwa), Brothers (Faisal & Andi),
and to the memory of my late Family-in-law
and other tsunami victims in Aceh.

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LIST OF ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
AI	Artificial Intelligence
ANOVA	Analysis of Variance
BET	Brunauer-Emmett-Teller
BP	Back-Propagation
CCC	Central Composite Circumscribed
CCD	Central Composite Design
CCF	Central Composite Faced
CCI	Central Composite Inscribed
DF	Degree of freedom
DOE	Design of Experiment
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
FGD	Flue Gas Desulfurization
FTIR	Fourier Transform Infrared
GHSV	Gas Hourly Space Velocity
ICDD	International Center for Diffraction Data
LM	Levenberg-Marquardt
MAQG	Malaysian Air Quality Guidelines
MFM	Mass Flow Meter
MOX	Malaysian Oxygen Berhad
MSE	Mean Square Error
NAAQS	National Ambient Air Quality Standards
NN	Neural Network
OSHA	Occupational Safety and Health Administration
PEL	Permissible Exposure Limit
RH	Relative Humidity
RHA	Rice Husk Ash
RSM	Response Surface Methodology
SCR	Selective Catalytic Reduction
SEM	Scanning Electron Microscopy

SNCR	Selective Non-Catalytic Reduction
SSE	Sum Square Error
TLV	Threshold Limit Value
US DOE	United State Department of Energy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
WHO	World Health Organization

LIST OF SYMBOLS

a	Activity (dimensionless)
a_o	Initial activity (dimensionless)
A	Sample coded for RHA/CaO sorbent preparation
A_o	Frequency or pre-exponential factor (min^{-1})
B	Sample coded for RHA_{raw}/CaO/NaOH sorbent preparation
C	Sample coded for $RHA_{600°C}$/CaO/NaOH sorbent preparation
C	Outlet concentration of gas (ppm or $kmol/m^3$)
C_a	Gas concentration in the particular gas cylinder (ppm or $kmol/m^3$)
C_b	Desired gas concentration from the particular gas cylinder (ppm or $kmol/m^3$)
C_o	Initial concentration of gas (ppm or $kmol/m^3$)
D	Sample coded for RHA/CaO/CeO_2 sorbent preparation
E_a	Activation energy (kJ/mol)
$\mathrm{F_s}$	Gas flow rate set by the mass flow controller (ml/min)
$\mathrm{F_t}$	Gas total flow rate (ml/min)
h	Hidden neuron
i	Index of data in SSE Equation (3.1)
i	Linear coefficient in second-order polynomial Equation (2.13)
j	Quadratic coefficient in second-order polynomial Equation (2.13)
k	Number of variables
k, k_1, k_2	Rate constants (min^{-1})
k_{ap}	Apparent rate constant (min^{-1})
k_o	Initial rate constant ($m^3\ kg^{-1}\ min^{-1}$)
k_d	Deactivation rate constant (min^{-1})
k_s	Surface rate constant (m/min),
m	Exponential coefficient in Equation (3.4)
n	Exponential coefficient in Equation (3.4)
Q	Volumetric flow rate (m^3/min)
R	Universal gas constant (kJ/mol.K)

R	Multiple Correlation Coefficient
R^2	Determination Coefficient
t	Reaction time (min)
T	Absolute temperature (K)
W	Sorbent mass (kg)
x	Coded value of hydration process variable
x_1	Coded term of hydration period (h)
x_2	Coded term of amount of RHA (g)
x_3	Coded term of amount of CaO (g)
x_4	Coded term of amount of water (ml)
x_5	Coded term of drying temperature (°C)
x_6	Coded term of RHA/CaO ratio (g/g)
x_7	Coded term of amount of NaOH (mol/l)
x_8	Coded term of CeO_2 loading (%)
x_9	Coded term of RHA type
x_i	Input/output data in Equation (3.2)
$x_{\max}$	Maximum value of data in particular variable in Equation (3.2)
$x_{\min}$	Minimum value of data in particular variable in Equation (3.2)
X	Conversion
y	Predicted responses
$y_{i,e}$	Experimental data in SSE Equation (3.1)
$y_{i,p}$	Prediction data in SSE Equation (3.1)

Greek symbols

α	Distance of the axial runs from the design center
β	Offset term (regression coefficient) in second-order polynomial Equation (2.13)
τ	Surface time (min/m)

PENYINGKIRAN SO_2 DAN NO DARIPADA GAS SEROMBONG YANG DISIMULASIKAN MENGGUNAKAN BAHAN SERAP ABU SEKAM PADI/CaO/CeO_2

ABSTRAK

Tujuan kajian ini adalah untuk menghasilkan bahan serap daripada abu sekam padi untuk penyingkiran serentak sulfur dioksida (SO_2) dan nitrogen oksida (NO). Kajian dicapai dengan menggunakan kaedah permukaan sambutan (RSM) yang digandingkan dengan rekaan pusat rencam (CCD). Pembentukan sebatian reaktif tertentu dalam bahan serap dipercayai sebagai faktor utama kepada kemampuan untuk menyerap SO_2 yang tinggi. Bahan serap abu sekam padi/CaO yang diisitepu dengan cerium dioksida (CeO_2) menunjukkan kemampuan penyerapan yang tertinggi terhadap SO_2/NO. Turut didapati bahawa model-model permukaan sambutan peringkat kedua bersama dengan model rangkaian neuron telah berjaya digunakan untuk meramalkan kemampuan bahan serap abu sekam padi/CaO/CeO_2 terhadap SO_2 dan NO, ia juga untuk mengesan dan mengesahkan keadaan optimum pembolehubah kaedah penyediaan bahan serap. Kehadiran NO dan SO_2 masing-masing mempercepatkan kemampuan bahan serap untuk menyerap SO_2 dan NO. Halaju ruang yang rendah menyebabkan kemampuan bahan serap terhadap SO_2 dan NO menjadi tinggi. Kelembapan relatif didapati meningkatkan kemampuan bahan serap rujukan terhadap SO_2, tetapi tidak terhadap NO. Suhu operasi yang tinggi adalah sangat sesuai untuk menyerap SO_2 dan NO. Tenaga pengaktifan dan faktor frekuensi bagi serapan SO_2 didapati masing-masing sebanyak 18.0 kJ/mol dan 7.37×10^5 sm^3/g.min. Manakala untuk tenaga pengaktifan dan faktor frekuensi bagi serapan NO adalah masing-masing sebanyak 5.64 kJ/mol dan 2.19×10^4 sm^3/g.min. Model kinetik pendeaktifan didapati menepati data eksperimen serapan SO_2/NO.

REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING RICE HUSK ASH/CaO/CeO_2 SORBENT

ABSTRACT

The purpose of this study was to develop a sorbent synthesized from rice husk ash (RHA) for simultaneous removal of sulfur dioxide (SO_2) and nitric oxide (NO). The study was achieved using Response Surface Methodology (RSM) coupled with Central Composite Design (CCD). The formation of specific reactive species in the sorbent are believed to be the key factor responsible for high SO_2 sorption capacity. RHA/CaO sorbent incorporated with cerium dioxide (CeO_2) displayed the highest SO_2/NO sorption capacities. It was also demonstrated that the second-order response surface models together with neural network (NN) model were used successfully to predict SO_2 and NO sorption capacities of the RHA/CaO/CeO_2 sorbents and as well as to locate and validate the optimum settings of the hydration process variables. The presence of NO and SO_2 accelerated the SO_2 and NO sorptions, respectively. A lower space velocity resulted in a higher SO_2 and NO sorptions. Relative humidity was shown to enhance the SO_2 sorption of the reference sorbent, but not for NO sorption. Higher operating temperatures were favored for SO_2 and NO sorptions. The activation energy and frequency factor for the SO_2 sorption were found to be 18.0 kJ/mole and 7.37×10^5 cm^3/g.min, respectively. Whereas the activation energy and frequency factor for the NO sorption, were estimated to be 5.64 kJ/mole and 2.19×10^4 cm^3/g.min, respectively. The deactivation kinetic model was found to give a very good agreement with the experimental data of the SO_2/NO sorptions.

CHAPTER 1

INTRODUCTION

Continuous increase in economic activities couple with the growing population throughout the world have led to a tremendous increase in energy consumption. The total world consumption of energy is projected to increase by 57 percent from 447 quadrillion Btu in 2004 to 702 quadrillion Btu in 2030, (U.S. DOE, 2007). Whereas in Malaysia, the energy consumption is considered relatively high in comparison to most developed countries and several advanced developing countries. In 2004, the total energy consumption in Malaysia was estimated about 2.5 quadrillion Btu (Country Analysis Briefs, 2007). In the near future, the energy consumption is expected to further increase especially in developing countries. This has led to a significant increase in industrial activity in recent times and consequently resulted in a massive increase of pollutants released to the atmosphere, water and soil, altering their composition, and causing harmful effects on the environment and human health. Although environmental problems was not an issue of interest to the world until the last century, some historical events have shown that the concern on the effect of certain man-made pollutants on human health have began some centuries ago (de Nevers, 2000).

Due to the harmful impact of air pollutants, regulatory agencies have enacted strict regulations to limit their emission. Air pollutants mainly come from discharges of gases from industry, motor vehicles and domestic wood burning (Cheremisinoff, 2002). The most widespread pollutants which are called primary pollutants are those emitted by an identifiable source which includes carbon monoxide (CO), oxides of nitrogen (NO_x), oxides of sulfur (SO_x), volatile organic compounds, hydrocarbons, metals and particulate matter (Kiely, 1997 & Schnelle and Brown, 2002).

1.1 Acidic Gas pollutants

Among the several air pollutants that contaminate our planet, SO_x and NO_x have received special attention due to the fact that these two pollutants have toxic and acidic characteristics. SO_x and NO_x have been linked to the formation of acid rain and many other undesirable environmental hazards (de Nevers, 2000). Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. Sunlight increases the rate of most of these reactions, which results in mainly sulfuric acid and nitric acid compounds. Acid rain can cause acidification of lakes and streams, damage to trees at high altitude, the acceleration of decay in buildings and poorer air quality. Acid rain also poses serious human health risks by contributing to heart and lung disorders such as asthma and bronchitis (Ayres *et al*., 2006).

The major sources of SO_x and NO_x are from the combustion of fossil fuels, *i.e.* coal and oil, in an industrial boiler for generating steam. In the U.S, about two-thirds of all SO_x and one-fourth of all NO_x comes from coal combustion, generally for electric power generation (Baukal, 2004; U.S. EPA, 2007). In Malaysia, most of the industrial combustion system is still highly dependent on fossil fuels to generate energy, *i.e.* meeting about 98% of Malaysia's energy requirements in 2003 (Amin, 2005).

The SO_x and NO_x formed during combustion process are then released into the environment together with the boiler flue gas. Typically, SO_x and NO_x in flue gases consists of more than 98% of sulfur dioxide (SO_2) (Probstein & Hicks, 2006) and more than 90% of nitric oxide (NO) (Zhu *et al.*, 2005). A typical characteristic of flue gas composition (Toole-O'Neil, 1998; Granite, *et al.*, 1999) is given in Table 1.1 in which the exact concentration would depend on the type of fossil fuel used.

Table 1.1. Typical flue gas composition.

Components	**Concentration**
SO_2	1000-2500 ppm
NO	500-1000 ppm
O_2	4-10 %
CO_2	16 %
H_2O	6 %
Hydrocarbons	10 ppm
Hg	1 ppb
N_2	Balance

1.1.1 Sulfur Dioxide (SO_2)

Sulfur dioxide (SO_2) belongs to the family of SO_x gases. SO_2 is a colorless, nonflammable, non-explosive acidic gas with a pungent odor and is used in a variety of chemical processes. It is highly soluble in water (85 g/l) with density of 2.618 g/l (25°C, 1 atm). Once released into the atmosphere, SO_2 can be oxidized to SO_3 and formed sulfuric acid in the presence of water (rain) (Baukal, 2004; Lide, 2005). The source of SO_2 can be classified as natural or man made. The natural source of SO_2 is resulted from, for example, volcanic eruption. The amount of SO_2 releases from volcanic eruption have been estimated to be roughly 13 x 10^6 tons/year, which is 5 to 10% of the quantity released by human activities (Brady *et al.*, 2000). In most urban areas, man-made contributions are of serious concern. Although most of SO_2 emission come from fossil fuels combustion, certain industrial processes (less than 10%) also emit SO_2, for example in the production of H_2SO_4, paper pulp, petroleum production, etc (Baukal, 2004).

The increasing usage of fossil fuels during this decade has resulted in an increase of world total SO_2 emission from 1995 to 2000 (Table 1.2). The evolution of SO_2 emissions varies from different regions in the world. Although there has been major progress in controlling SO_2 emissions in some countries, including Malaysia, however, the global threat from acid rain still exist. Further increase in SO_2 emission is estimated to occur especially in Asian countries, with China being the highest SO_2 emitter (25.5 million tons) in comparison to any country in the world in 2005 (Delfs, 2007).

Table 1.2. Total SO_2 and NO_x emissions (million tons)
(World Resources Institute, 2007).

Year	**Worldwide**		**Malaysia**	
	SO_2	**NO_x**	**SO_2**	**NO_x**
1995	142	99	0.43	0.53
2000	150	127	0.42	0.73

Since SO_2 gas is one of the most hazardous pollutants released into the environment, threshold limit or emission standard have been introduced in many countries. Various types of standards are used to regulate the emission of SO_2, the SO_2 removal rate, the sulfur content in the fossil fuels or the requirement for control technology. However, the standard based on SO_2 emission/air quality standard is most commonly used. Table 1.3 shows the SO_2 emission limits for coal-fired power plants in various countries and standards/recommendation made by some agencies/ institutions.

Table 1.3. Various threshold limits for SO_2 and NO_x.

Pollutants	**Countries/ Institutions**	**Coal-fired power plant limits (ppm)**[1]	**Standards (air quality/ambient) (ppm)**
SO_2	Malaysia	350	
	USA	260	
	Australia	70	
	Germany	140	0.021 (annual average)[2] 0.049 (24 h average)[2]
	Japan	50-200 (plant specific)	
	Belgium	400	
	MAQG[3]		0.037 (24 h average)
	WHO[4]		0.007 (24 h average) 0.175 (10 min)
	NAAQS[5]		0.028 (annual average) 0.128 (24 h average)
	ACGIH-TLV[6]		2
	OSHA-PEL[6]		5
NO	ACGIH-TLV[6]		25
	OSHA-PEL[6]		25
NO_2	Germany[2]		0.024 (24 h average)
	MAQG[3]		0.112 (1 h average)
	WHO[4]		0.014 (annual average) 0.07 (1 h average)
	NAAQS[5]		0.035 (annual average)
	ACGIH-TLV[6]		3
	OSHA-PEL[6]		5

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

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

1.1.2 Nitrogen Oxides (NO_x)

Nitrogen oxides (NO_x) is the generic term for a group of highly reactive gases, all of which contain nitrogen and oxygen in varying amounts, mainly consist of nitric oxide (NO), nitrogen dioxide (NO_2) and a small fraction of nitrous oxide (N_2O). On one hand, NO is a colorless gas with density of 1.226 g/l (25°C, 1 atm) and has very low solubility in water and NO is a precursor to the formation of NO_2. On the other hand, NO_2 is a reddish-brown, highly reactive gas and is a strong oxidizing agent with a density of 1.880 g/l (25°C, 1 atm). NO_2 is extremely soluble in water and actually reacts with water to produce nitric acid (HNO_3) and NO. N_2O is not a common air pollutant, but has been proven to be a contributing factor toward global warming (de Nevers, 2000; Baukal, 2004; Lide, 2005). The source of NO_x present in the air may come from natural processes (including lightning, volcanic eruptions and bacterial action in the soil) or from man-made activities. The NO_x emission from man-made activities is of a particular environmental concern. NO_x is formed during most combustion processes by one or more of the following mechanism (de Nevers, 2000; Baukal, 2004); (1) thermal NO_x, resulting from oxidation of molecular nitrogen in the combustion air at high temperature (2) prompt NO_x, resulting from reaction between molecular nitrogen, oxygen and hydrocarbon radicals by the relatively fast reaction, and (3) fuel NO_x, resulting from oxidation of chemically bound nitrogen in the fuel.

NO and NO_2 are the most abundant man-made NO_x in urban areas resulted from various activities, such as in the combustion of fossil fuels in stationary sources (heating, power generation) and in motor vehicles (internal combustion engines). Other sources are industrial processes such as manufacture of nitric acid and explosives, smoking, gas-fired appliances and oil stoves. The predominant NO_x emitted by combustion processes is NO. More than 95 % of NO_x emitted from diesel engine is in the form of NO (Fritz & Pitchon, 1997).

It was estimated that the global NO_x emissions generated by man-made activities increase from 99 million tons in 1995 to 127 million tons in 2000 as shown in Table 1.2. In the absence of any abatement strategies, this total NO_x emission will increase steadily within the next decade. Apart from that, McIlvaine (U.S. research company) predicted that NO_x emission which come from coal-fired plants around the world will rise from 26 million tons in 2005 to about 30 million tons by 2020. From that, Asia will account for 22 million tons in 2020 or 73% of the total world NO_x emission from coal-fired plants (McIlvaine Co., 2006). The negative effects of NO_x emission have also resulted in a number of threshold limit or emission standard being implemented as shown in Table 1.3.

1.2 Acidic Gas Control Technology – An Overview

Based on the information mention in sections 1.1.1 and 1.1.2, it is proven that SO_2 and NO_x emissions from both stationary and mobile sources can cause various adverse effects on human health and on the environment. Therefore, SO_2 and NO_x emissions, especially resulted from combustion process, need to be reduced considerably. Consequently, control of acidic gas pollutants has become increasingly stringent all over the world. Presently, SO_2 and NO_x are being removed using various types of control technology. Nevertheless, the most common technology used today is still by two separated system to remove these acidic gas pollutants although both gases are from the same source.

Generally, the technological alternatives to reduce SO_2 from combustion process can be grouped into three major categories; pretreatment/pre-combustion control, process & combustion modification, and post-combustion control. In pretreatment control, sulfur content in fossil fuel is usually removed prior to combustion (fuel cleaning) or fuel with lower content of sulfur (fuel switching) is used to reduce SO_2 emission in power generation. While in process and combustion modification, several strategies can be implemented. One strategy is to use an alternative method for generating the energy needed for daily factory operation, for example to use electrical energy instead of burning fossil fuel. The other alternative is to burn high-sulfur coal in a fluidized bed combustor (where the bed contains limestone particles) instead of using a traditional combustor/boiler. However, most of these methods for controlling SO_2 emission are not viable alternatives for industrial combustion processes due to uneconomical constraints (in pretreatment control) and the systems are either too complex or still in the development state (in process & combustion modification) (Baukal, 2004). As a result, attention is usually focused on SO_2 post-treatment methods, which can also be referred as Flue Gas Desulfurization (FGD) processes.

A large number of FGD processes have been developed and are expected to play an important role in reducing SO_2 emission from power plants. FGD methods can be classified according to the end products formed in the process. The methods are divided into regenerable and non-regenerable processes, where in the former case, the SO_2 removed is recovered. In the latter case, also known as once-through (throwaway) methods, the end product is mainly a solid waste material which has to be disposed off. Presently, regenerable FGD process is not much being used in comparison to non-regenerable process due to relatively higher capital and operating expenses (Srivastava & Josewicz, 2001). Both regenerable and non-regenerable processes can be further categorized into subgroups depending on the reactive phase in which SO_2 is removed, *i.e.* dry, semi-dry or wet processes. Wet FGD process is currently most widely used in the industries using limestone slurry ($CaCO_3$) as sorbent. These methods are highly efficient in removing SO_2 (92 - 96 %), however they require a large space for installation, large volume of water, producing huge amount of sludges which must be disposed off and thus leading to high capital and operating expenses (Ishizuka *et al*., 2000b; Lin *et al*., 2003). Due to the drawbacks of wet-type methods, researches have shifted their attention on the dry FGD methods. Most of the non-regenerable dry FGD methods utilize calcium-based chemicals (limestone, lime & hydrated lime) because they produce relatively safe and stable end product (Berland *et al*., 2003; Galos *et al*., 2003).

Meanwhile, control of the NO_x emission is presently achieved mainly through modification of the combustion processes to prevent the formation of NO_x or by removing NO_x in the flue gas (post-treatment) (de Nevers, 2000; Baukal, 2004). There are several combustion control technologies for NO_x removal, such as low excess air operation, fuel and air staged burner, low NO_x burners, reduced air preheat, water injection, and flue gas recirculation. Post-combustion flue gas treatment includes selective catalytic reduction (SCR) and selective noncatalytic reduction (SNCR). In the SCR process, a gaseous mixture of ammonia (NH_3) and air is injected into an exhaust stream with the presence of a catalyst within a specific temperature range (approximately 230-600°C). The NO_x and NH_3 will react on the catalyst surface to form nitrogen and water. The NO_x removal efficiency depends on the type of catalyst, effective surface area of catalyst, residence time, amount of ammonia added, NO_x concentration in the flue gas and the usage of the catalyst. In the SNCR process, NH_3 or urea-based sorbents are added into an exhaust stream, whereby flue gas temperature is between 870-1200°C. The NO_x will be reduced to nitrogen and water without involving catalyst. The efficiency of this process is a function of the flue gas temperature, residence time and type/amount of reagent used. Table 1.4 shows the advantages and disadvantages of the various methods of NO_x reduction.

Table 1.4. Methods of NO_x reduction (de Nevers, 2000; Baukal, 2004).

Method	Advantage	Disadvantage
Low NO_x burners	low operating cost	limited NO_x reduction
Staged burners	low operating cost	limited NO_x reduction
Flue gas recirculation	low operating cost	limited NO_x reduction
Selective catalytic reduction	high NO_X reduction (70% to 95%)	high capital and operating costs
Selective non-catalytic reduction	lower capital and operating costs	limited NO_x reduction (25-50%)

1.3 Solid Waste from Combustion Process

Apart from producing air pollutants, industrial combustion processes also leave behind a huge amount of solid waste in the form of ash. For example, coal combustion in coal-fired power plant will leave behind a residue consisting of organic matters, which is not completely burned, known as coal ash. During the combustion process, the coal ash is distributed into two parts, fly ash (collected by air pollution control equipment through the stack gas pass) and bottom ash (collected from the bottom of the boiler unit) (Lee, 2004). In another example, some agricultural industries, *e.g.* palm oil processing mill and rice mill, use their own biomass solid waste as boiler fuel to produce steam for electricity generation to run their production processes. In palm oil processing mill, large amount of biomass solid waste is being produced in forms of fiber, shell and empty fruit bunch (Mahlia *et al*., 2001; Sumathi *et al*., 2008). Based on the specific properties of the solid biomass, especially those with lower moisture content, fiber and shell are being used as boiler fuel and as a result of that, ash is produced as another solid waste at the end of the combustion process. Similar to that, rice industry also produced large quantity of rice husk and rice straw as a by-product of rice cultivation or rice milling processes (Lu, 1994; Bronzeoak, 2003). Rice husk and rice straw has traditionally been used as an ingredient in ruminant and poultry feeds. However, in modern rice milling industry, rice husks are used as a source of fuel for parboiling and electricity generation, which will also produce an additional solid waste in the form of ash. Characteristics of these ashes vary depending on the combustion conditions.

1.3.1 Solid Waste from Rice Production

Rice is one of the world's most important crops. Rice is grown on every continent except Antarctica and covers 1 % of the earth's surface. It is a primary source of food for billions of people, and ranks second to wheat in terms of area and production. Table 1.5 shows that more than 600 million tons of rice paddy is produced worldwide in 2006 (FAO Statistical Databases, 2008). Asia accounts for more than 90 % of the world's production and consumption of rice because of its favorable hot and humid climate (Hossain, 1997). The demand for rice is projected to increase, primarily due to rapid population growth, especially in Asia.

Table 1.5. Total rice production and by-product estimation (tons) (FAO Statistical Databases, 2009).

	2000			**2007**		
	World	**Asia**	**Malaysia**	**World**	**Asia**	**Malaysia**
Paddy production	598,893,695	545,481,533	2,140,800	651,742,616	591,719,883	2,231,000
Rice husk[1]	119,778,739	109,096,307	428,160	130,348,523	118,343,977	446,200
Rice husk ash (RHA)[2]	21,560,173	19,637,335	77,069	23,462,734	21,301,916	80,316

Assumption (Bronzeoak, 2003): [1]Husk = 20% paddy production and [2]RHA = 18% husk.

Lately, with the increase in rice crop yields and cropping intensity, the management of rice by-products (wastes) has now become an important issue. The major by-products from rice mill are rice straw and rice husk that are obtained after the harvesting and production processes as shown in Table 1.6. These by-products have a relatively high caloric value and therefore, one possible means of economically utilizing these solid wastes is by combusting it as fuel to produce energy via steam power plants. The energy generated can then be used for their production processes. Its usage as a source of fuel will lead to other benefits such as saving in the cost of fuel, reducing the disposal problem and also promoting energy sustainability as it is a renewable resource. However, due to the lower moisture content of rice husk, it is the preferred fuel for parboiling in comparison to rice straw (Table 1.6). Apart from that, as shown in Table 1.6, the major constituents of rice straw and rice husk are cellulose, hemicellulose, lignin and crude protein varying with the variety, climate and geographic location of paddy growth. Therefore, the ashes produced from burning rice husk can be exploited as a useful by-product (Bronzeoak, 2003), known as rice husk ash (hereinafter referred to as RHA). The ash obtained from combustion at moderate temperature contains approximately 90-96% of silica in amorphous form (Table 1.6).

Table 1.6. Selected properties of rice straw and rice husk (George & Ghose, 1983; Lu, 1994; Bronzeoak, 2003).

	Rice straw	**Rice husk**
Generated	Harvesting	Paddy milling
Quantity	2-8 tons/ha	20-22%(w) of paddy
Moisture content	60% (wet basis) 10-12% (dry weather)	10%
Density	75 kg/m^3 (loose straw) 100-180 kg/m^3 (packed form)	100-150 kg/m^3 200-250 kg/m^3 (ground)
Carbohydrate component (average)	Cellulose (43%) Hemicellulose (25%) Lignin (12%) Crude protein (3-4%)	Cellulose (35%) Hemicellulose (25%) Lignin (20%) Crude protein (3%)
Caloric value	14-16 MJ/kg (14% moisture content)	14-16 MJ/kg (10% moisture content)
Ash	22% (silica 83%)	16-22% (silica 90-96%)

1.3.2 Rice Husk Ash (RHA)

Typically, for every 100 kg of paddy milled, about 20 kg (20%) of husk is produced. The husk contains about 75% organic volatile matter and after being burnt in boilers, about 16-22% of ash (RHA) will be generated. Rice husk is unusually high in ash content compared to other biomass fuels. The type of ash varies considerably according to the burning technique. The silica in RHA undergoes structural transformations depending on the conditions (time, temperature, etc) of the combustion process. At combustion temperature of 550-800 °C, amorphous ash is formed, while at higher combustion temperatures, crystalline ash is formed. These two types of silica (amorphous and crystalline) have different properties as shown in Table 1.7.

Table 1.7. Properties of silica.

	Type of Silica (SiO_2)	
	Amorphous	**Crystalline**
Combustion of rice husk (Bronzeoak, 2003)	550-800 °C	Above 800 °C
Structure (Lujan & Ary, 1992)	• Having an unstructured molecular arrangement. The atoms and molecules are randomly linked, forming no pattern. • X-rays are scattered randomly and no discrete reflections are seen.	• Having a highly structured molecular arrangement. The atoms and molecules form a three-dimensional, repeating pattern, or lattice. • Show discrete reflections in X-ray diffraction from the internal planes formed by the orderly pattern of atoms.
Pozzolanic reaction (Lin *et al.*, 2003)	More reactive in participating in the pozzolanic reaction.	Less reactive.
Solubility (neutral pH, 25°C) (Sahachaiyunta *et al.*, 2002)	100-120 mg/l	5-6 mg/l
Example (Lujan & Ary, 1992)	Glass, diatomaceous earth, fly ash, precipitated silica, silica gel, fused silica and silica fume.	Crystalline silica can take several forms: quartz (most common), cristobalite, tridymite, etc.
Health effect (Lujan & Ary, 1992)	Silicosis (lung disease), TB, lung cancer, and scleroderma (not classifiable as to its carcinogenicity to humans (Group 3)).	Carcinogenic to humans (Group 1).

It was estimated that more than 22.8 million tones of RHA was produced worldwide in 2006, an increased from 21.5 million tons in 2000. In Malaysia alone, more than 77 thousand tones of RHA is produced annually (Table 1.5). At the moment, RHA is used as fertilizer (TropRice, 2004), cement substitute and other construction materials (Tuts, 1994; Mehta, 1994; Jauberthie *et al*., 2003; Nehdi *et al*., 2003), alternative source for active silica production (Yalcin & Sevinc, 2001; Kalapathy *et al*., 2000; Liou, 2004), vulcanizing rubber (Siriwandena *et al*., 2001), oil adsorbent (Kalapathy & Proctor, 2000; Chou *et al*., 2001) and an insulator during steel manufacturing (Bronzeoak, 2003; TropRice, 2004). Despite the various possible utilization of RHA, there is still abundance of RHA available which is not being completely utilized (as shown in Table 1.5).

1.4 Problem Statement

Lately, the combustion of solid fuel to generate electricity has caused the emission of SO_2 and NO_x to the environment. Thus, the control of SO_2 and NO_x emissions has become an issue of great importance to governmental regulatory agencies and general public due to their negative effect towards the environment and human health. This has led and in a way, forcing countries around the world (including Malaysia) to impose a more stringent regulation on the release of these air pollutants into the atmosphere. The need to lower the emissions of these pollutants creates a high demand for technical solution that can meet the environmental regulations but yet are economically attractive. Currently, wet-method of FGD technology based on limestone, lime, or sodium carbonate are the most widely employed in the industries due to its high efficient in removing SO_2. However, this technology is ineffective for NO_x removal, due to the low solubility of nitric oxide in calcium based solution. Thus, another separate system is used for the removal of NO_x, leading to the usage of two separate systems to remove these pollutants. For example, the industries would requires the SNOX process of Haldor Topsoe which combine the wet-gas sulfuric acid process and the selective catalytic reduction (SCR) process for the removal of SO_2 and NO_x, respectively (Kohl & Nielsen, 1997; Schoubye *et al.*, 2002). The need of this two separate systems make the overall gas cleaning system very expensive and unfavorable to small-medium industries (SMI). Therefore, lately attention has been given to the development of simultaneous removal of SO_2 and NO_x using dry-methods due to the drawbacks of wet-type methods. Nevertheless, acidic gas sorption capacities of dry-methods are generally lower than those achieved with wet technologies. Consequently, enhancing the sorption capacities of dry sorbent toward SO_2 and NO_x has been a challenging task. Apart from generating pollutants, combustion of solid fuel also produces voluminous ash as the by-product. Since air pollutants (such as SO_2 and NO_x) and ashes (such as RHA) are produced simultaneously from industrial combustion processes, an attractive and economical solution to this problem is to somehow utilize the ash to sorb these air pollutants.

1.5 Research Objectives

The main objective of this study is to develop a dry-type sorbent material synthesized from RHA for simultaneous removal of SO_2 and NO. At the same time, the undertaken study aims to achieve the following measurable objectives.

1. To identify the key factor for high SO_2 sorption capacity in sorbent prepared from RHA/CaO.
2. To investigate the use of additives to enhance SO_2 sorption capacity of RHA/CaO sorbent.

3. To investigate the use of metal oxides for simultaneous removal of SO_2 and NO and to determine the optimum preparation variable of RHA/CaO/CeO_2 sorbent.
4. To observe the effect of various sorber operating parameters affecting sorption capacity of RHA/CaO/CeO_2 sorbent.
5. To generate the deactivation kinetic models based on breakthrough curves.

1.6 Scope of Study

In this study, the term sorption (by sorbent) was used to depict surface phenomenon which may be either absorption or adsorption, or a combination of both. Since the major NO_x gas emitted by combustion processes is NO, therefore, in this study NO gas was used in the simulated flue gas. As mentioned in section 1.3.1, the composition of rice husk varies with the variety, climate and geographic location of paddy growth, therefore the composition of RHA will also be affected. For that reason, this study is only limited to a batch of RHA obtained from Kilang Beras & Minyak Sin Guan Hup Sdn.Bhd., Nibong Tebal, Penang. In this study, RHA-based sorbent was prepared using RHA and calcium-based materials (CaO, $Ca(OH)_2$, $CaCO_3$) using water hydration method. Since there are many variables affecting the sorbent preparation, however, this study focused only on the effect of seven variables (hydration period, drying temperature, amount of RHA/Ca-based, amount of water, additive used, metal loading and type of RHA). These variables are carefully selected based on the previous studies and some preliminary experiments. In the sorbent preparation steps, design of experiment (DOE) of Central Composite Design (part of Response Surface Methodology design) was applied to study the effect of sorbent preparation variables and to develop mathematical models for the acidic gas sorption capacity in order to diminish the drawback of conventional method which is laboratorious and time-consuming. In certain part of this study, neural network (backpropagation network) was used to compare the accuracy of predicted model obtained by DOE of Central Composite Design.

In this study, initially RHA/calcium-based sorbent was synthesized for SO_2 removal. Then, this sorbent was incorporated with selected metal oxides for simultaneous removal of SO_2 and NO_x. Simulated flue gas (containing 2000 ppm of SO_2, 500 ppm of NO, 10% of O_2, water vapor (50 % humidity) and N_2 as the balance with the total flow rate of 150 ml/min) was used to study the performance of prepared sorbent. The removal activity of the sorbents toward acidic gases can be expressed in many terms. Nevertheless, in this study, it was decided to use the term acidic gas sorption capacity expressed by the weight of SO_2/NO captured from the flue gas per gram sorbent (Peterson & Rochelle, 1988; Garea *et al.*, 1997a; Liu & Shih, 2004b). The amount of SO_2/NO captured by the sorbent was recorded continuously until it shows negligible activity (the outlet SO_2/NO concentration becomes the same as the inlet concentration). In some cases, the sorbent activity was also reported using breakthrough curves. Once the specific sorbent obtained under optimum condition for maximum removal of SO_2/NO, it will be used to study the effect of various reactor operating conditions.

The reaction between the prepared sorbent and SO_2/NO are very complicated due to the complex composition of the sorbent. Therefore in this study, it was decided to use the simplified deactivation kinetic model against other models that usually contain large number of adjustable parameters related to the pore structure, product layer and pore diffusion resistances as well as the surface sorption rate parameters. In addition, it is complicated to incorporate them without having to perform lengthy computer programs. The breakthrough curves data obtained for both SO_2 and NO sorptions was fitted to deactivation kinetic model using nonlinear regression analysis.

1.7 Layout of the Thesis

This thesis consists of five chapters. Chapter 1 (Introduction) present a brief introduction to the harmful effect of air pollutants especially SO_2 and NO_x, an overview of the current SO_2/NO_x control technology and a short summary on the solid waste (ashes) production from combustion process. This section also gives the problem statements that justify the basis and rationale on the necessity of this research study followed by the objectives of this research. In the last section of this chapter, the overall content of this thesis is summarized in the thesis layout.

Following this introductory chapter is Chapter 2 (Literature Review) that elaborates some information concerning SO_2, NO_x and simultaneous SO_2/NO_x control technologies. Some background information about specific problems to be addressed in this research and as well as the experimental design and methods that are relevant to this research were also given in this chapter.

Chapter 3 (Materials and Methods) describe in detail all materials and chemical used in the present study. This is followed by methods of sorbent preparation and characterization procedures. The experimentation tools used (statistical design of experiment) together with neural network approach are then elaborated in detail in this section. This chapter also presents details of experimental set-up and procedure used for sorbent sorption studies.

Chapter 4 (Results and Discussion) is the core of this thesis and is divided into six sections. In the first section, preliminary study on the removal of SO_2/NO was carried out using raw materials and modified sorbents. Identifying key factor for SO_2

removal using RHA-based sorbents was performed in the next section. In the third section, improvement of RHA-based sorbents toward SO_2/NO was investigated using various additives and metal oxides addition. In the subsequent section, an attempt to optimize the sorbent preparation variables was carried out using statistical design of experiment and neural network approach. In the fifth section, the effect of various operating conditions (such as feed concentration of SO_2/NO, space velocity, relative humidity and operating temperature) on the sorbent sorption capacities were conducted. In the last section of this chapter, the breakthrough curves data of RHA-based sorbents was fitted to deactivation kinetic model.

Chapter 5 (Conclusions and Recommendation) gives the concluding remarks of all the findings obtain throughout this study and recommendations for future research based on their significance and importance related to the current study.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews background information on the various approaches, methods and materials that are currently being used to control SO_2 and NO_x emissions. Particular interest is given to research findings on the development of dry-type processes at low temperature that appear to be the most promising technique for the removal of SO_2 and also simultaneous removal of SO_2 and NO_x. The fundamental of deactivation kinetic model is also presented in this chapter. Finally, the experimental design, method and concept that are being used in this study are presented.

2.1 Dry Method for SO_2 Control Technologies

Within the past two decades a realization has evolved on the need to remove SO_2 from flue gases that are produced from industrial processes. This gas represents the main fraction of anthropogenic sulfur emissions from industrial processes. There are several alternatives for reducing SO_2 emission, along with existing technologies for removal of SO_2 from stack gas of industrial processes. High stack chimneys have been successfully used in the past decades for dispersing pollutants and keeping ambient concentrations low enough to prevent SO_2 emissions from being harmful. However, the total amount of SO_2 released and subsequently the overall increase in ambient concentration over broad zones can be problematic. Another method for reducing ambient concentrations of SO_2 is by using fuels with lower sulfur content, however, fuels with lower sulfur content are usually more scarce and expensive than the traditional fuels with high sulfur content. Subsequently, a better solution is to develop a variety of technologies to eliminate or reduced SO_2 emission. Most of the technologies available currently for removing SO_2 emission are based on post-treatment methods, which can be referred to as Flue Gas Desulfurization (FGD) processes.

Most of FGD processes involve the contact between gas stream containing SO_2 with sorbents in the form of liquid or solid. Upon sorbing SO_2, a final product of either liquid (known as the wet-method) or dry solid (known as the dry-method) is usually obtained. However, due to some drawbacks of wet-method FGD systems, such as large space required for installation, large volume of water used and high capital and operating expenses (Ishizuka *et al*., 2000b; Lin *et al*., 2003), researchers had shifted their attention to dry-method for SO_2 removal. Various types of solid sorbent/catalysts are being used in dry-method FGD, such as calcium-based sorbent, sodium-based sorbents, activated carbon, metal oxides, zeolites, sorbent from waste-derived siliceous materials, and a combination among these sorbents/catalysts. Apart from that, dry-method FGD has been basically studied for temperature in the lower range(< 200°C) (Karatepe *et al*., 1998; Garea *et al*., 2001; Krammer *et al*., 2002; Ho *et al*., 2002; Renedo & Fernandez, 2002; Gupta *et al*., 2004; Bausach *et al*., 2005; Lee *et al*., 2005), medium range (300-600°C) (Konttinen *et al*., 1997; Wang & Lin, 1998; Fernandez *et al*., 1998a; Fernandez *et al*., 1998b; Shi & Xu, 2005; Hou *et al*., 2005; Li *et al*., 2006) and higher range (>700°C) (Allen & Hayhurst, 1996; Al-Shawabkeh *et al*., 1997; Wang & Bjerle, 1998; Ersoy-Mericboyu & Kucukbayrak, 1998; Yan *et al*., 2003; Dasgupta *et al*., 2003). However, most of the study only focused on dry-FGD technology at lower range of temperature with the presence of water vapor due to lower energy requirement and favorable economic concerns.

2.1.1 Calcium Sorbent

One of the earliest attempts in dry FGD methods is the utilization of raw calcium materials, *i.e.* lime (CaO), hydrated lime ($Ca(OH)_2$ and limestone ($CaCO_3$). Ho *et al.* (1996) reported the use of reagent grade $Ca(OH)_2$ as a sorbent on the reaction with SO_2 in a fixed bed reactor. The gas mixture comprised of SO_2, CO_2, O_2, H_2O and N_2. It was found that, in the presence of CO_2, the sulfation and carbonation reactions took place simultaneously until $Ca(OH)_2$ ceased to react. The sulfation rate and final total conversion were greater than those for the case without CO_2. On the contrary, Garea *et al.* (1996) shows that no effect of CO_2 was observed on the FGD process at low temperature (< 100°C). However, CO_2 concentration was found to have a significant impact on desulfurization at medium temperatures (> 300°C). This result was also supported by Krammer *et al.* (1997) which has found that the presence of O_2 and/or CO_2 do not show any significant influence on the SO_2 removal activity at low temperature. Furthermore, the relative humidity (RH) of the gas has a major impact on the reactivity of the sorbent. The product of the reaction was detected to be calcium sulfite hemihydrate. However, the activity of the sorbent is not promising as the removal activity of the $Ca(OH)_2$ drops significantly after a conversion of around 9%. This observation was believed to be due to the plugging of pores by the reaction products.

Chu *et al.* (2000) investigated FGD process using calcium sorbent and silica sand in a bubbling fluidized bed reactor. The calcium sorbent consist of 64.5 % CaO, 27% $Ca(OH)_2$, 4.5% $CaCO_3$ and other minor compound. The effects of the various operating parameters of the FGD on SO_2 removal efficiency and calcium sorbent conversion in the fluidized bed were investigated. It was found that fluidized bed temperature from 40 to 65°C had negligible effect on the activity of the sorbent.

Higher relative humidity leads to higher calcium conversion and higher SO_2 removal efficiency. Furthermore, calcium sorbent with smaller particle size leads to lower calcium conversion but higher SO_2 removal efficiency. Apart from that, lower superficial gas velocity resulted in higher SO_2 removal efficiency and calcium conversion. Although 100% SO_2 removal efficiency can be obtained for a period of about 10 min with appropriate operating conditions, however the final solid conversion hardly goes beyond 30%.

Krammer *et al.* (2004) studied the reactivity of commercial $Ca(OH)_2$ as a sorbent toward SO_2. The experiment was carried out in a fixed bed reactor by exposing the sorbent to a gas stream (3900-4150 ppm SO_2) with a high relative humidity (34.5 – 86.8 %). In their study, this exposure is referred to as activation. The relative humidity of the gas was determined from the temperature of the water bath and the reaction temperature in the fixed bed reactor. The reactivity of $Ca(OH)_2$ towards SO_2 was significantly enhanced during activation.

Bausach *et al.* (2005) examined the reaction between $Ca(OH)_2$ and SO_2 at low temperature in a fixed bed reactor. The effect of relative humidity, temperature and NO_x and SO_2 concentration on the capacity of solid sorbent were evaluated in terms of breakthrough curves. It was observed that relative humidity exerted a significant influence on the SO_2 removal capacity of the sorbent, while temperature has only a slight influence. The presence of NO_x also enhances the capacity of $Ca(OH)_2$ towards SO_2 removal. Concerning the effect of SO_2 concentration, which is another major factor affecting the SO_2 removal capacity on solid conversion, different behaviors was obtained depending on the relative humidity (RH). It was reported that no influence was observed at 30% RH, however, a slight negative effect was observed above 30% RH.

In a more recent work, Liu and Shih (2006) revealed the reaction between $Ca(OH)_2$ and SO_2 under conditions similar to those in the bag filters of a spray-drying FGD system under the presence of different combinations of the gaseous species. The major findings of this study were that the presence of NO_x/O_2 enhanced the oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} in the water layer sorbed on the $Ca(OH)_2$ surface and the formation of deliquescent salts of calcium nitrite and nitrate. The enhancement effect was more pronounced when the relative humidity was above $\geq 70\%$, at which the salts deliquesced.

2.1.2 Sodium-based Sorbents

Sodium-based sorbents is another type of dry sorbent used to remove SO_2 from flue gases. Most of the research on sodium-based sorbents has been conducted mainly using sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and trona ($NaHCO_3$. $Na_2.CO_3.2H_2O$). The potential by-product resulted from the reaction between sodium-based sorbent and SO_2 is mainly sodium sulfate (Na_2SO_4) which has a wide application in photographic, detergent, chemical, glass and paper industries (Garrett, 2001).

Keener and Davis (1984) studied the reaction of SO_2 with Na_2CO_3 and $NaHCO_3$ over various temperatures and particle sizes. The results for both Na_2CO_3 and freshly formed Na_2CO_3 obtained from the decomposition of $NaHCO_3$ are quite different. They postulated that this might be due to high level of reactivity on the surface of Na_2CO_3 that is instantaneously formed following the thermal decomposition of $NaHCO_3$. It was also suggested by Keener and Khang (1993) that $NaHCO_3$ can also react with SO_2 directly at temperatures lower than 67°C. In a more recent work, Wu *et al*. (2004) had shown that temperature is the major factor