MATHEMATICAL MODELING OF SIMULTANEOUS REMOVAL OF SO_2 AND NO USING SORBENT SYNTHESIZED FROM ASH

by

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LIST OF ABBREVIATIONS

ACGIH	American Conference of Governmental Industrial Hygienists
ADP	Adenosine diphosphate
AMG	Algebraic Multigrid
API	American Petroleum Institute
BET	Brunauer-Emmett-Teller method
CFA	Coal fly ash
CVFE	Control volume finite element
$DeNO_x$	Denitrification
$DeSO_x$	Desulfurization
DWT	Discrete Wavelet Transform
ESP	Electrostatic precipitators
FDM	Finite Difference Method
FEM	Finite element method
FGD	Flue gas desulfurization
FGDN	Flue gas denitrification
FV	Finite volume
FVE	Finite volume element
FVM	Finite Volume Method
Iso	Isothermal
JSM – 35 CF	Model of SEM equipment
MAQG	Malaysian Air Quality Guidelines
MG	Multigrid
MOL	Method of lines
MSc	Master
MSU	Michigan State University
NAAQS	National Ambient Air Quality Standards
Non	Non-isothermal
ODE	Ordinary differential equation
OSHA	Occupational Safety and Health Administration
PDE	Partial differential equation

PEL	Permissible Exposure Limit
PSS	Pseudo steady-state
QSARs	Quantitive structure-activity relationships
RAD-C	Model of XRD equipment
RHA	Rice husk ash
RMSE	Root mean squared error
SI	International System of Units
SCM	Unreacted shrinking core model
SCO	Selective catalytic oxidation
SCR	Selective catalytic reduction
SEM	Scanning electron microscope
SIM	Sharp Interface Model
SCNR	Selective noncatalytic reduction
TLV	Threshold Limit Value
TOF	Turn over frequency
TST	Transition state theory
US	United State
USS	Unsteady-state
VODE	Variable-coefficient Ordinary Differential Equation solver
WHO	World Health Organization
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

A	Reactant A
A_s	Transversal bed section in Model 1 (m^2)
A_1	Arbitrary constant in Eq. (3.45)
A_c	Cross-sectional area of the tube in Model 2 (m^2)
b	Stoichoimetric coefficient
B	Reactant B
B_1	Arbitrary constant in Eq. (3.45)
c	Order of reaction in Eq. (3.27)
C_A	Concentration of gas A
C_{AS}	Concentration of gas A at surface of pellet
C_{NO}	Concentration of NO (mol/m^3)
C_{SO}	Concentration of SO_2 (mol/m^3)
C_s	Concentration of SO_2 (ppm)
d_p	Diameter of spherical particle (m)
D	Coefficient of diffusion (constant, m^2/s)
D_e	Coefficient of diffusion (m^2/s)
D_o	Pre-exponential constant for coefficient of diffusion in Model 2 (m^2/s)
D_{AB}	Gas diffusivity
D_{eo}	Pre-exponential constant for coefficient of diffusion in Model 1 (m^2/s)
E	Activation energy for gas-solid diffusion in Model 2 (J/mol)
E_a	Activation energy for reaction (J/mol)
E_{diff}	Activation energy for gas-solid diffusion in Model 1 (J/mol)
E_{gas}	Activation energy for gas-phase diffusion (J/mol)
F	Fitting parameter for Eq. (3.25)
F_3	Coefficient of plugging in for Eq. (3.72) (J/mol)
F_5	Coefficient of plugging in for Eq. (3.74) (J/mol)

F_7	Coefficient of plugging in for Eq. (3.75) (J/mol)
g	Order of reaction in Eq. (3.24)
k	Rate constant (m/s)
k_g	Rate constant for gas phase (m/s)
k_{go}	Pre-exponential constant for rate constant of gas phase (m/s)
k_o	Pre-exponential constant for rate constant (m/s)
L_o	Length of reactor (m)
m	Order of reaction in Eq. (3.22)
M	Molecular weight (g/gmol)
n	Flow rate of feed gas (mol/s)
P	Solid product
r	Pore radius (m)
r_A	Reaction rate of gas A (mol/m^2.s)
r_A''	Reaction rate of gas A (mol/m^2.s)
r_s	Reaction rate (mol/m^2.s)
R	Specific gas constant (J/mol.K)
Re	Reynolds number
RH	Relative humidity
S	Solid particle
Sc	Schmidt number
S_e	Specific surface area (m^2/g)
Sh	Sherwood number
t	Reaction time (s)
U	Superficial molar average velocity through the bed (m/s)
V_R	Volume of reactor (m^3)
w	Weight of sorbent (g)
X	Conversion
Y	Dimensionless SO_2 concentration
z	Length position (m)
Z	Dimensionless length position
ε	Porosity

ρ	Density of gas (kg/m^3)
τ	Tort (s)
ρ_c	Density of sorbent CeO_2/CaO/RHA (kg/m^3)
γ	Surface heterogeneity parameter (J/mol)
γ_o	Pre-exponential constant (J/mol)
φ	Dimensionless variable
λ	Dimensionless variable
ϕ	Thiele modulus
η	Internal effectiveness factor
Ω	Overall effectiveness factor
ε_b	Porosity of reaction bed in Model 2
υ_o	Flow rate (m^3/s)
υ	Kinematic viscosity (m^2/s)
α	Pre-exponential constant
ρ_B	Density of sorbent CaO/$CaSO_4$/CFA (mol/m^3)

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PEMODELAN MATEMATIK BAGI PENYINGKIRAN SERENTAK SO_2 DAN NO DENGAN MENGGUNAKAN BAHAN SERAP YANG DISINTESIS DARIPADA ABU

ABSTRAK

Pemodelan matematik dan penyelidikan gunaan menggabungkan kekuatan daripada matematik gunaan, kajian kinetik dan analisis berangka untuk menerbitkan, menganalisis dan menyelesaikan model matematik bagi masalah yang kompleks. Kesemua teknik ini digunakan dalam kajian ini untuk menyelesaikan satu tindak balas gas pepejal kompleks bagi penyingkiran sulfur dioksida (SO_2) dan nitrogen oksida (NO) daripada gas serombong menggunakan bahan serap yang disintesis daripada abu. Secara umumnya, kompleksiti masalah ini merangkumi tiga peringkat kajian analisis kinetik iaitu makro-, meso- dan mikro-skopik. Model 1 telah dibangunkan berdasarkan satu kadar tindak balas global antara SO_2 dan abu terbang batu arang/CaO/$CaSO_4$ (bahan serap kering). Secara spesifik, ungkapan fasa gas eksponen, ungkapan fasa pepejal struktur dan model penyusutan inti tanpa tindakbalas yang diubahsuai (SCM) dengan penambahan terma faktor penutupan permukaan ($f(\theta)$) telah digunakan bagi tujuan pembangunan model. Meskipun kombinasi kajian kinetik makro- dan meso-skopik yang diimplementasikan dalam Model 1 memberikan "*root mean squared error*" (RMSE) yang rendah dengan nilai 4.77% (antara data eksperimen dengan jangkaan), tetapi sisihan data jangkaan yang tinggi pada kandungan kelembapan relatif yang tinggi (pada 70%) telah diperhatikan. Oleh kerana itu, Model 2 yang berdasarkan mekanisma tindak balas yang terdiri daripada 15 tindak balas asas telah dicadangkan untuk dibangunkan bagi mengkaji dengan lebih lanjut proses penyahsulfuran/penyahnitrifikasi ($DeSO_x$/$DeNO_x$) serentak oleh bahan serap yang dihasilkan daripada CeO_2/CaO/abu sekam padi pada

aras mikroskopik. Dengan bantuan mekanisma tindak balas yang dicadangkan, Model 2 mendedahkan aspek-aspek tersirat yang tidak boleh dijelaskan oleh model heterogen tipikal (contoh, SCM atau SCM yang diubahsuai) seperti selektiviti tindak balas, modulus Thiele yang mentakrifkan langkah penentu kadar, urutan langkah-langkah tindak balas yang menerangkan proses $DeSO_x$/$DeNO_x$ dan kedua-dua faktor keberkesanan dalaman dan keseluruhan yang mewakili terma resapan. Nilai RMSE yang munasabah sebanyak 6.50% telah diperolehi bagi Model 2 dengan membandingkan data daripada 34 kajian eksperimen dan melebihi 2514 titik data dengan data jangkaan. Oleh itu, keputusan ini menunjukkan bahawa 15 langkah tindak balas yang dicadangkan dalam mekanisma sebelum ini adalah boleh dipercayai pada tahap keyakinan yang tinggi. Tambahan pula, kestabilan mekanisma tindak balas yang dicadangkan dalam Model 2 diuji dengan membina semula Model 1 dengan menggunakan mekanisma yang sama dan model baru dinamakan Model 3. Model 3 dibangunkan dengan menggunakan langkah dan methodologi yang sama seperti dalam Model 2. Keputusannya, Model 3 didapati dapat menjangkakan data eksperimen dengan nilai RMSE yang lebih kecil iaitu 3.11%. Oleh itu, ini tidak hanya membuktikan bahawa model matematik yang berasaskan mekanisma adalah kaedah yang lebih sesuai dalam mewakili tindak balas heterogen gas pepejal tetapi juga memperkukuhkan lagi kestabilan mekanisma tindak balas yang dicadangkan dalam Model 2. Tambah lagi, Model 3 kini boleh digunakan untuk menjelaskan sisihan data jangkaan yang didapati dalam Model 1 dengan penjelasan sumbatan liang oleh penukaran CaO, pembentukkan $CaSO_4.2H_2O$ dan penghabluran $Ca(OH)_2$.

MATHEMATICAL MODELING OF SIMULTANEOUS REMOVAL OF SO_2 AND NO USING SORBENT SYNTHESIZED FROM ASH

ABSTRACT

Mathematical modeling and applied analysis combine the strengths of applied mathematics, kinetic studies and numerical analysis to derive, analyze and solve mathematical models of complex problems. These techniques were used in this study for solving a complex heterogeneous gas-solid reaction for the removal of sulfur dioxide (SO_2) and nitrogen oxide (NO) in flue gas using siliceous sorbent. Generally, its complexities encompassed three level of studies; macro-, meso- and micro-scopic kinetic analysis. Model 1 was developed based on a global reaction rate between SO_2 and coal fly ash/CaO/$CaSO_4$ (dry sorbent). Specifically, exponential gas phase expression, structural solid phase expression and modified un-reacted shrinking core model (SCM) with the inclusion of surface coverage factor ($f(\theta)$) were used for model development. Although the combinations of macro- and meso-scopic kinetic study implemented in Model 1 was found to give low root mean squared error (RMSE) of 4.77% (between experimental and predicted data), but strong discrepancy of data prediction at high relative humidity (at 70%) was observed. Therefore, Model 2 was subsequently developed based on a proposed reaction mechanism which consists of 15 elementary reactions in order to further study the microscopic level of simultaneous desulfurization/denitrificantion ($DeSO_x$/$DeNO_x$) process using sorbent synthesized from CeO_2/CaO/rice husk ash. With the help of the proposed reaction

mechanism, Model 2 unravels some hindering aspects in which typical heterogeneous models (i.e. SCM or modified SCM) are unable to explain such as selectivity of reaction, Thiele modulus that defines rate limiting step, sequence of reaction steps that depicts $DeSO_x$/$DeNO_x$ processes and both internal and overall effectiveness factors that re-present diffusion-dependence term. An acceptable RMSE value of 6.50% was obtained for Model 2 by comparing data from 34 experimental runs and over 2514 data points with predicted data. Thus, this result assures that the 15 reaction steps proposed in aforementioned mechanism is truly reliable at a very high confidence level. In addition, the stability of the reaction mechanism proposed in Model 2 was tested by reconstructing Model 1 with similar mechanism and naming it Model 3. Model 3 was developed using the same procedures and methodology applied in Model 2. As the result, Model 3 was able to predict the experimental data with a smaller RMSE value of 3.11%. Therefore, this does not only proved that the mechanism-based mathematical model is a better method in expressing the complex heterogeneous gas solid reaction but also inevitably affirms the stability of the reaction mechanism proposed in Model 2. In addition, Model 3 was then able to explain the data prediction discrepancy found in Model 1 that is because of pores plugging due to the conversion of CaO, formation of $CaSO_4.2H_2O$ and crystallization of $Ca(OH)_2$.

LIST OF PUBLICATIONS

Journal:

Henry, F., Lee, K.T., Fernando, N. & Mohamed, A.R. Kinetic model of coal fly ash/Ca based sorbent for flue gas desulphurization at low temperatures. *Journal of Brazilian Chemical Engineering* (Submitted)

Henry, F., Lee, K.T., Fernando, N. & Mohamed, A.R. Mathematical modeling and mechanism study of simultaneous removal of SO_2 and NO using sorbent synthesized from CeO_2/CaO/Rice Husk Ash (RHA). *American Institute of Chemical Engineers* (Submitted)

CHAPTER ONE

INTRODUCTION

Flue gas is a gas that exits to the atmosphere via a duct in a chimney for smoke and waste gases. Quite often, it refers to the combustion exhaust gas produced at power plants. Its compositions will usually contain significant amount of N_2, O_2, CO_2 and water vapor, but also pollutants such as nitric oxides (NO_x), sulfur dioxide (SO_2), and fly ash (Eichwald et al., 1997). For instance, the combustion product gas resulting from the burning of fossil fuels are combusted with ambient air (as differentiated from combustion with pure oxygen) is referred. Since dry ambient air contains roughly (by volume) 78.08% N_2, 20.95% O_2, 0.93% Ar, 0.038% CO_2, and trace amounts of water vapor, on average around 1% (Granite et al., 1999; Toole-O'Neil, 1998), hence, the largest part of the flue gas from most fossil fuel combustion is uncombusted nitrogen. The next largest part of the flue gas is carbon dioxide which can be as much as 10 to 15 in volume percent or more of the flue gas. This is closely followed by water vapor (in volume) created by the combustion of hydrogen compound in the fuel with atmospheric oxygen. Apart from that, a typical flue gas from the combustion of fossil fuels will also contain some very small amount of nitrogen oxides, sulfur dioxide and particular matter. Nitrogen oxides are derived from nitrogen in ambient air as well as from any nitrogen-containing compounds in the fossil fuel while sulfur dioxide is derived from any sulfur-containing compounds in the fuels. Particulate matter is composed of very small particles of solid materials and very small liquid droplets which give flue gases their smoky appearance.

Nowadays, a large amount of flue gas that is emitted to the ambient atmosphere comes from steam generators in power plants and process furnaces in large refineries, petrochemical and chemical plants, and incinerators. These industries burn huge amounts of fossil fuels and subsequently release undesired end product as flue gas to ambient atmosphere. **Table 1.1** shows the total amount of flue gas typically generated by burning fossil fuels such as natural gas, fuel oil and coal. The data in **Table 1.1** were obtained by stoichoimetric calculations (Zumdahl, 2005). Besides, it is of interest to note that the total amount of flue gas generated by coal combustion is only 10 percent higher than the flue gas generated by natural gas combustion.

Although environmental problems were not an issue of interest to the world until the last century, some historical events have shown the impact of certain man-made pollutants on human health particularly pollutant present in combustion flue gas. Due to the harmful impact of air pollutants, it must be removed before the flue gas is emitted to the atmosphere. In this regard, many countries in the world have started to impose emission standard toward combustion flue gas. Emissions standards are requirements that set specific limits to the allowable amount of pollutants that can be released to the environment. Many emissions standards focus on regulating pollutants released from industry and power plants. Frequent policy alternatives to emissions standards are technology standards (which mandate the use of a specific technology) and emission trading.

Table 1.1: Exhaust flue gas generated by combustion of fossil fuels (In SI metric units and in USA customary units) (Zumdahl, 2005)

Combustion Data	**Fuel Gas**	**Fuel Oil**	**Coal**
Fuel properties:			
Gross caloric value, MJ/Nm^3	43.01		
Gross heating value, Btu/scf	1,093		
Gross caloric value, MJ/kg		43.50	
Gross heating value, Btu/gallon		150,000	
Gross caloric value, MJ/kg			25.92
Gross heating value, Btu/pound			11,150
Molecular weight	18		
Specific gravity		0.9626	
Gravity, ^{o}API		15.5	
Carbon/hydrogen ratio by weight		8.1	
Weight % carbon			61.2
Weight % hydrogen			4.3
Weight % oxygen			7.4
Weight % sulfur			3.9
Weight % nitrogen			1.2
Weight % ash			12.0
Weight % moisture			10.0
Combustion air:			
Excess combustion air, %	12	15	20
Wet exhaust flue gas:			
Amount of wet exhaust gas, Nm^3/GJ of fuel	294.8	303.1	323.1
Amount of wet exhaust gas, scf/10^6 Btu of fuel	11,600	11,930	12,714
CO_2 in wet exhaust gas, volume %	8.8	12.4	13.7
O_2 in wet exhaust gas, volume %	2.0	2.6	3.4
Molecular weight of wet exhaust gas	27.7	29.0	29.5
Dry exhaust flue gas:			
Amount of dry exhaust gas, Nm^3/GJ of fuel	241.6	269.3	293.60
Amount of dry exhaust gas, scf/10^6 Btu of fuel	9,510	10,600	11,554
CO_2 in dry exhaust gas, volume %	10.8	14.0	15.0
O_2 in dry exhaust gas, volume %	2.5	2.9	3.7
Molecular weight of dry exhaust gas	29.9	30.4	30.7

Note: Nm^3 at 0^{o}C and 101.325 kPa, and scf at 60^{o}F and 14.696 psia.

Table 1.2 shows the standards used to regulate the emissions of nitrogen oxides (NO_x) and sulfur oxides. SO_2 and NO have received special attention due to the fact that these two pollutants have toxic and acidic characteristics. Both of these pollutants have been linked to the formation of acid rain and many other undesirable environmental hazards. In the following section, a more detail description on SO_2 and NO will be given followed by various technologies available for the removal of SO_2 and NO.

Table 1.2: Various threshold limits for SO_2 and NO_x.

Pollutant	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)
	AGGIH-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)
	ACGGIH-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 Sulfur Dioxide (SO_2)

Sulfur dioxide (also sulphur dioxide) is the chemical compound with the formula SO_2. It is a gas produced by volcanoes naturally and in various industrial processes by human civilization particularly during combustion of fossil fuel in which its detail information on its properties are listed in **Table 1.3** (Perry and Green, 1997). Since coal and petroleum often contain sulfur compounds, their combustion generates sulfur dioxide. Further oxidation of SO_2, usually in the presence of a catalyst such as NO_2, forms H_2SO_4, and thus acid rain. This is one of the causes for concern over the environment impact due to the use of these fossil fuels as power sources.

Table 1.3: Physical and chemical properties of SO_2 (Perry and Green, 1997).

Properties	Value
Molecular Formula	SO_2
Molar mass	64.07 g/mol
Appearance	Colorless gas
Density	2.551 g/L (gas) 1.46 g/cm^3 (liquid, -10^{o}C)
Melting Point	-75.5^{o}C, 198 K, -104^{o}F
Boiling Point	-10.0^{o}C, 263 K, 14^{o}F
Solubility in water	22.97 g/100 mL (0^{o}C) 11.58 g/100mL (20^{o}C) 9.4 g/100 mL (25^{o}C)
Solubility	Very soluble in acetone, methyl isobutyl ketone, acetic acid, alcohol soluble in sulfuric acid
Acidity (pKa)	1.81
Viscosity	0.403 cP (0^{o}C)

Note: Properties were inspected under 1 atm and 25^{o}C

Although SO_2 is the deleterious source that causes acid rain, its role as a main reactant in several useful processes is undeniable. For example, SO_2 is used as a precursor to produce sulfuric acid, a preservative to dry apricots, an antibiotic and antioxidant in winemaking to protect wine from spoilage by bacteria and oxidation, a reductant to decolorize substances, a refrigerant and a reagent or solvent in laboratory solvent that has been widely used for dissolving highly oxidizing salts. Nevertheless, a high concentration of SO_2 that violated the emission standard will cause acid rain, disease, difficulty in breathing and even premature death. Therefore, reduction in emission of such air pollutant is required for industrial operations. In this standpoint, capture and removal of SO_2 is accomplished by devices known as flue gas desulfurization unit or commonly scrubbers.

1.2 Nitric Oxide (NO)

Nitric oxide or nitrogen monoxide is a chemical compound with chemical formula NO. It is a colorless gas and its detail physical and chemical properties of NO are reviewed and listed in **Table 1.4** (Perry and Green, 1997). This gas is an important signaling molecule in the body of mammals, including humans, and is an extremely important intermediate feedstock in the chemical industry. It is also an air pollutant produced by cigarette smoke, automobile engines and power plants. Although NO has relatively few direct uses, it is produced in a massive scale as an intermediate in the Ostwald process during the synthesis of nitric acid from ammonia. For example, in 2005, US alone produced 6M metric tons of nitric acid (Chemical and Engineering News, 2006).

In pharmacology, nitric oxide is considered an anti-anginal drug: it causes vasodilatation, which can help with atherosclerosis by improving blood flow to the heart. However inhaling too much of NO gases will result in direct tissue or vascular collapse associated with septic shock, whereas chronic expression of NO is associated with various carcinomas and inflammatory conditions including juvenile diabetes, multiple sclerosis, arthritis and ulcerative colitis. Hence, monitoring of such deleterious gases in the atmosphere is an ongoing issue that must be given careful attention. The technique used in controlling the emission of NO in power plant is known as flue gas denitrification.

Table 1.4: Physical and chemical properties of NO (Perry and Green, 1997).

Properties	**Value**
Molecular formula	NO
Molar mass	30.006 g/mol
Appearance	Colorless gas
Density	1.269 g/cm^3 (liquid) 1.3402 g/L (gas)
Melting point	-163.6^{o}C, 110 K, -262^{o}F
Boiling point	-150.8^{o}C, 122 K, -239 ^{o}F
Solubility in water	7.4 ml/100ml (STP)
Solubility	Soluble in alcohol, CS_2

Note: Properties were inspected under 1 atm and 25^{o}C

1.3 Acid Gas Control Technology

Generally, the technological alternatives to reduce SO_2/NO from combustion process can be grouped into three major categories; pretreatment/pre-combustion control, process & combustion modification, and post-combustion control. In pretreatment control, for instance, 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 acidic gases emission are not viable alternatives for industrial combustion processes due to economical constraints (in pretreatment control) and the systems are either too complex or still in the development state (in process & combustion modification). As a result, attention is usually focused on SO_2/NO post-treatment methods, which can also be referred as Flue Gas Desulfurization (FGD) and Flue Gas Denitrification processes (FGDN) respectively.

1.3.1 Flue Gas Desulfurization

Lately, international legislation around the world has imposed the need for installing FGD’s unit in power plants especially coal-fired power plants to control SO_2 emissions. There are currently many technologies available for FGD and it categorized into three main groups which are dry sorbent injection, semi-dry and wet processes.

1.3.1 **(a) Wet Scrubbers (Wet Method)**

The wet scrubber process is by far the most common Flue Gas Desulfurization method use today and can achieve a sulfur dioxide removal efficiency rate of 99% (Dalton, 1990). This process involves spraying the flue gas with aqueous slurry of lime (CaO) or limestone ($CaCO_3$) in a spray tower or absorber. The SO_2 is removed through a series of chemical reactions between the slurry and SO_2 to produce calcium sulfate and calcium sulfite. The resultant slurry has traditionally been disposed off by mixing with fly ash from the power plant and a fixative lime and discarded in a landfill. However if a forced oxidation step is included either in the scrubber process or afterwards, the slurry can be turned entirely into gypsum and can then be sold and utilized in the manufacturing of wallboard, cement, and agricultural soil amendments.

1.3.1 (b) Spray Dry Scrubbers (Semi-Dry Method)

Spray dry scrubbers is the second most common method of Flue Gas Desulfurization, achieving an efficiency rating between 93-97% (Jozewicz and Rochelle, 1986). This method uses a water based sorbent containing lime or calcium oxide that is sometimes referred to as lime milk. This lime slurry is atomized in a reactor vessel in the form of an extremely fine spray of droplets. The heat from the flue gases entering the vessel evaporates the water from the slurry and the newly hydrated lime reacts with SO_2 to form a dry mixture of calcium sulfate/sulfite. The benefits of this process include the elimination of any water treatment process due to complete evaporation. However, this technology is limited to volume of flue gases produced from power plants in the 200 MW range and requires the use of the more expensive sorbent lime rather than limestone.

1.3.1 (c) Sorbent Injection (Dry Method)

The third method of Flue Gas Desulfurization is the Sorbent Injection method. The Sorbent Injection involves spraying a dry sorbent, usually limestone or hydrated lime ($Ca(OH)_2$) into the flue gases in the upper part of the furnace. The sorbent reacts with SO_2 and produces gypsum as a byproduct, which is later captured in a fabric filter or via electrostatic precipitators (ESP) together with unused sorbent and fly ash. Nevertheless, efficiency for this process can be as low as 50% (Tischer, 1991). If humidification of the flue gases is added to the process and the sorbent is sprayed further along in the flue gas duct where temperatures have cooled considerably, the sulfur dioxide removal efficiency can be boosted to 80%. The advantages of this method include low capital and operating costs, ease of retrofitting and operating, and the non-requirement to handle slurry or wastewater.

1.3.2 Flue Gas Denitrification

Unlike the removal of SO_2, the technology available to remove NO is mainly post-combustion. In post-combustion flue gas treatment includes selective catalytic reduction (SCR) and selective noncatalytic reduction (SCNR) (de Nevers, 2000; Baukal, 2004). In 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^{o}C) (Dahlan et al., 2009). NO and NH_3

will then react on the catalyst surface to form nitrogen and water. The NO removal efficiency depends on the type of catalyst, effective surface area of catalyst, residence time, amount of ammonia added, NO concentration in the flue gas and the usage of the catalyst. In the SCNR process, NH_3 or urea-based sorbents are added into an exhaust system, whereby flue gas temperature is between 870-1200^oC (Dahlan et al., 2009). NO 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.

1.3.3 Combined Technologies of $DeSO_x/DeNO_x$

Aimed at reducing both deleterious gases, a so-called combined desulfurization/denitration ($DeSO_x/DeNO_x$) processes have received great attention recently. Being the utmost advantage, it saves the volume of sorbent by simultaneously removal of both flue gases with single particle compared with conventional SCR/FGD separate systems. Researchers had applied this technology in dry FGD process and study its performance. In one study, the use sorbent prepared from CeO_2/CaO/RHA was investigated (Dahlan et al., 2009). Basically, CeO_2 is a rare earth metal which is classified as catalyst. However, CaO doped with CeO_2 gave it an ability to donate his free oxygen electron rather than use the oxygen from atmosphere during oxidation process. Therefore, CeO_2 exists partly as catalyst and reactant at the same time. Due to the excess oxygen's supply, regeneration step of CeO_x to CeO_2 became feasible and overwhelmed. As the result, CeO_2 will be classified as catalyst rather than a reactant in this study. It is strongly believed that CeO_2 acts as a selective catalytic oxidation (SCO) agent that aggressively oxidized

NO molecule to a less harmful species, NO_2. On the other hand, CaO represents the dry-flue gas desulfurization reagent where it can react with SO_2 and formed a solid product by chemisorptions process. Moreover, additional of RHA into the preparation of the sorbent has unambiguously increased its surface areas greatly. Phenomenon of such steep increment in surface area is attributed to the pozzolanic reaction between CaO and RHA. Although the threshold of aforementioned method is still at the development stage, it has shown much potential to render FGD process in a more effective in cost and removal efficiency compared with conventional dry FGD system.

1.4 Problem Statement

Lately, international legislation around the world has imposed the need for installing FGD's unit in power plants especially coal-fired power plants to control SO_2 emissions. There are currently many technologies available for FGD but the most common commercial technology adopted is the wet-process method with lime stone derivatives as absorbent. However, this technology requires high investment cost that might not be economically viable for small scale power plants. On the other hand, recent studies have shown that calcium based-sorbent prepared from various siliceous materials such as coal fly ash, rice husk ash and oil palm ash can be used effectively to remove SO_2 especially for small scale application. This dry-process was proven to be significantly cheaper and simpler than the current wet-process with less space requirement, easier to retrofit and produces dry solid product, which is easier to handle (Qi *et al.*, 2007). In addition to this, the silicious calcium based dry sorbent can also be easily modified by impregnation metals for the simultaneous removal of NO. However, lower efficiency for SO_2 removal using these silicious sorbent in dry-process is still hindering this technology from being completely commercialized.

In order to improve the removal efficiency, a combined $DeSO_x/DeNO_x$ technique has been applied to simultaneously remove both deleterious gases of SO_2 and NO by using single particle of sorbent whereas in this study, performances of a sorbent prepared from CeO_2/CaO/RHA were studied. Somehow, these removal processes are predicted to be proceeding in a complex concurrent and consecutive mechanism. Therefore, the mechanism of these strong coupling reactions still remained as a controversial topic and some endless unambiguous postulation. To further facilitate the combined $DeSO_x/DeNO_x$ technique, efforts are required to study the kinetics of this process thoroughly (i.e. study on effect of physical properties such as temperature, concentration and relative humidity toward its reaction rate). With a better understanding regarding the complex synergism, the kinetics could be elucidated in details and computed the output accurately. Therein, optimization steps would be easier and boosting the development of a better sorbent with such knowledge.

1.5 Research Objectives

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

1. To develop mathematical model based on a coal fly ash (CFA)/Ca based sorbent for flue gas desulfurization at low temperatures (Model 1).
2. To develop mathematical model based on a mixed oxides sorbent synthesized from CeO_2/CaO/Rice Husk Ash (RHA) for simultaneous removal of SO_2 and NO (Model 2).
3. To propose a mechanism of elementary reactions for simultaneous removal of SO_2 and NO.
4. To study the effect of various parameters affecting sorption capacity of both sorbents (on Model 1 and 2).
5. To examine the robustness of the mechanism proposed in Model 2.

1.6 Scope of Study

In this study, two mathematical models were developed based on two different types of sorbents to remove flue gases which are $CaO/CaSO_4/CFA$ and $CeO_2/CaO/RHA$ respectively. Nevertheless, both models are used to provide the frameworks for describing the rates at which a chemical reaction occurs and enables us to relate the rate to a reaction mechanism that illustrates how the molecules react via intermediates to eventual the end product. With this information, the rate can then be related to the macroscopic process parameters such as concentration, pressures and temperatures. Hence, kinetics study provides a tool to link the microscopic world of reacting molecules to the macroscopic world of industrial reaction engineering.

The main objective of this research is to study the kinetic of the reaction between SO_2/NO and silicious sorbent. However it is a very broad field of study that is closely interwoven with numerous other scientific disciplines. This becomes immediately evident if we realize that $DeSO_x/DeNO_x$ process as a phenomenon that encompasses many level of study. The first level of investigation is on reactions at the elementary level involving the breaking of bonds in reactants and the formation of bonds in products. Generally, such analysis is categorized as microscopic kinetic analysis and is the domain of spectroscopy, computational chemistry and kinetics and mechanism on the level of elementary reaction steps.

The next level of study is that of small active particles, with typical dimensions of between 1 and 10 nm (Qi et al., 2007), and inside the pores of support particles which is related to mesoscopic kinetic analysis. For this level, the points of interest are the size, shape, structure and composition of the active particles, in particular of their surfaces, and how these properties relate to sorption reactivity. This is the domain of sorbent preparation, characterization, testing on the laboratory scale, and mechanistic investigations. Transport phenomena such as the diffusion of molecules inside pores may affect the rate at which products form and become an important consideration at this level. Much academic research as well as exploratory work in industry occurs on this scale.

Lastly, the most common researches in engineering field is the microscopic level in which reactors set up as 25 cm test reactor in the laboratory or the 10 m high reactor vessel in an industrial plant whereas the sorbent forms the heart of the FGD unit (Jiang et al., 2006). Nevertheless catalytic/noncatalytic gas-solid reaction as a discipline is only one of many other aspects of reaction engineering, together with, for example, the design of efficient reactors that are capable of handling high pressure, offer precise control of temperature, enable optimized contact between reactants and catalyst and removal of products, are resistant to corrosion, make optimum use of energy resources, and are safe during operation.

In describing the kinetics of catalytic/noncatalytic reactions on the scale of reactors, extrinsic factors dealing with the mass and heat transport properties of reactants and products through the reactor bed are as important as the intrinsic reactivity of the molecules reacting at the active site. The sorbent’s mechanical stability, sensitivity to temperatures, are important in addition to its intrinsic properties such as activity and selectivity. This research will encompass all the three level of study whenever appropriate.

1.7 Organization of the Thesis

This thesis consists of five chapters and each chapter covers different scope of study. Chapter 1 (Introduction) presents a brief introduction on flue gas especially SO_2 and NO. It gives the definition of flue gas, selected certain properties of exhaust gas from combustion, standard of flue gas emission and general information of SO_2 and NO. Apart from that, several techniques of flue gas removal are discussed leading to the problem statement that justifies the basis and rationale on the necessity of this research study followed by the objectives of this research. At the end of this chapter, the overall contents of this thesis are summarized in this thesis layout.

Chapter 2 (Literature Review) elucidates information concerning mathematical modeling of gas-solid reactions. All information given in this chapter is based on the study accomplished by other researchers over the past decade of hard work. It includes some reviews on two types of gas-solid reactions classified as catalytic and noncatalytic reaction. Nevertheless the core of this research accounts on how a mathematical model is developed. Thus, in this chapter, a detail survey on the available model nowadays that defined the gas-solid reaction of flue gas removal and the fundamental of theories involved were discussed as well. Finally, a summary is given to address the background information of this present study and points out some specific problems which is about to be solved in chapter 3.

Chapter 3 (Theoretical) describes in detail on how a mathematical model is developed from a fundamental theory. There are 2 models developed based on 2 sets of experimental data separately. For Model 1, the mathematical model is derived based on the study of coal fly ash/Ca based sorbent and for Model 2, the mathematical model is derived based on the study of a mixed oxides sorbent of CeO_2/CaO/RHA. Generally, the mathematical model developed takes into account many levels which are macro-, meso- and micro-kinetic study. From these different standpoints of consideration, a methodology of solution is presented at the end of this chapter to solve all the partial differential equations.

Chapter 4 (Results and Discussion) is divided into 3 main sections. In the first section, preliminary study of a global mathematical model on the removal of SO_2 using coal fly ash/Ca based sorbent was carried out (Model 1). Generally this global mathematical model only covers the first two level of research which is macro- and meso-kinetic studies. Next section, a second mathematical model (Model 2) that includes macro-, meso- and micro-kinetic studies was discussed. This second mathematical model is based on the independent study of simultaneous removal of SO_2 and NO using CeO_2/CaO/RHA sorbent. The ultimate specialty of the second model is the mechanism proposed. It explains the microscopic world of elementary reactions for sorption activity. Finally, the last part of this chapter is to check the robustness of the mechanism proposed in Model 2. This is done by developing Model 3. Model 3 is developed by using the mechanism proposed in Model 2 and applies it to the experimental data used for developing Model 1.

Chapter 5 (Conclusion and Recommendation) gives the concluding remarks of all the findings obtained throughout this research based on their significance and importance related to this current study. Recommendations for future research are also given.

CHAPTER TWO

LITERATURE REVIEW

2.1 Mathematical Modeling of Gas-Solid Reaction

Gas solid reaction is classified as heterogeneous reaction since the main reactants are in a different phase or due to formation of solid products with gaseous/aqueous reactants. Åström and Eykhoff (1974) defined a mathematical model as a representation of the essential aspects of an existing system (or a system to be constructed) which presents knowledge of that system in usable form. In short, mathematical modeling uses mathematical language to describe a system. It is used to explain the phenomena happening within the system and the models can take many forms, including but not limited to dynamical systems, statistical models, differential equations, or even game theoretic models. These and other types of models can overlap with a given model involving a variety of abstract structures.

Therefore in this review, fundamental mathematical models which are normally used to simulate multiple heterogeneous reactions with a complex set of physicochemical and thermal phenomena are presented. In a broad sense, the reaction of a porous solid particle with a gaseous species is a fairly complex process in which complete analysis needs consideration of a large number of physical and chemical rate processes. It involves mass transport of gaseous reactants and products in the surrounding gas phase, mass transport in the interior of the porous particle, and reaction on its external and internal surface area. On top of that, for exothermic reaction systems, it may also be necessary to consider the effects of heat transport in the surrounding gas phase or even in the interior of the porous particle. These processes, however, are not unique to non-catalytic gas-solid reactions but are encounter in other reactive systems, catalytic gas-solid reactions for instance. Generally, gas solid reaction are sub-categorize to catalytic solid gas reaction and non-catalytic gas solid reaction.

2.2 Catalytic Gas-Solid Reaction

Most solids in gas-solid reactions act as heterogeneous catalysts and catalyze reactions with reactants in the gas phase. For example, in the study carried by Courtois *et al*.(2007), finely confined cerium oxides serves as a catalyst for the oxidation of nitric oxide. In principle, CeO_2 provides an active site where elementary reactions take place. The specific activity of such site is scientifically of great interest when comparing the importance of different metals or geometric configurations. Therefore, Turn Over Frequency (TOF) is used as the criterion for catalyst activity measurement. It is defined as the number of reactant molecules that are converted over this site per second. However the industry is more concern on the activity per unit volume of catalyst. Having a high dispersion is important, but provided the particles must have a high number of the desired sites. Apart from that, durability and selectivity also form important considerations. It is not favorable to have a high conversion of reactants if it leads to a wide range of different products. This would result in expensive separation procedures for isolating the relevant products. Thus, an ideal catalyst must be able to give high conversion and high selectivity simultaneously.

Normally heterogeneous catalysts are typically “supported,” which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost (Rodriguez, 2003). Sometimes the support is merely a surface upon which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Nevertheless, heterogeneous catalytic gas-solid reaction has several aspects in common with gas-solid reaction un-catalyzed by porous solid; but the ultimate difference is that the solid matrix inside the particle does not change its chemical composition with time for catalytic gas-solid reaction.

2.3 Non-catalytic Gas-Solid Reaction

Non-catalytic gas-solid reaction consider porous particle of solid reactant introduced in a gaseous environment containing the gaseous reactant. Generally, gaseous species *A* diffuses through the surrounding gas phase into the pores and reacts with solid particle *S* according to the reaction

$$S(solid) + A(gas) + \ldots \rightarrow P(solid) + \ldots \quad (2.1)$$

The reaction initiates on the external and internal surface of the porous solid particle. Because of the formation of solid product *P*, a progressively thicker solid product layer covers the reaction surface through which the gaseous reactant *A* must diffuse in order to reach the unreacted solid. At any time *t*, therefore, the porous medium is characterized by two receding surfaces, the unreacted-reacted solid interface (reaction surface) and the solid-gas interface (pore surface) (Chorkendorff and Niemantsverdriet, 2007).

Examples of non-catalytic gas-solid reactions include coal gasification, roasting of pyrites, and pyrolysis. Such reactions also find wide applications in some auxiliary operations in air pollution control. DoǦu (1981) reported that the pore structure variations during gas-solid reactions and the initial pore structure of the solid reactant played a very important role in the kinetics of SO_2 removal. The initial pore size distribution of the solid reactant (CaO) was found to affect both the diffusion resistance of the gaseous reactant (SO_2) through the pores and the active surface area of the solid. It was found that diffusion is the rate limiting step in the reaction which is inversely proportional to the particle size. The maximum fractional conversion of CaO to $CaSO_4$ decreases with increase in temperature owing to faster pore mouth closure, while the initial rate increases. The reaction rate constant decreases exponentially with time owing to formation of a $CaSO_4$ layer on the CaO surfaces. Although it was shown that the experimental results agree well with the analytical expressions derived from the proposed model, evolution of the pore structure of the solid causes most of the difficulties encounter in their mathematical modeling because of the physicochemical changes that the reacting solid undergoes. **Table 2.1** summarizes mathematical models of non-catalytic gas solid reaction that are currently developed and summarized into six different domain which are reaction state, thermodynamic status, components involved, diffusivity, solution method and model classification accordingly.

Table 2.1: Summary of mathematical model available for gas-solid reactions.

Authors	Year	PSS/USS	Non/Iso thermal	Single/ multiple	Diffusivity	Solution method	Model
Yagi and Kunni	1955	PSS	Iso	Single	Constant	Analytical	SCM
Shen and Smith	1965	PSS	Iso	Single	Constant	Analytical/numerical	SCM
Wen	1968	PSS	Iso	Single	Constant	Analytical/numerical	SCM
Ishida and Wen	1968	PSS	Non	Single	Exponential	Analytical	SCM
Calvelo and Cunningham	1970	PSS	Iso	Single	Effective	Analytical	SCM
Szekely and Evans	1970	PSS	Iso	Single	Constant	Analytical	Grain
Szekely and Evans	1970	PSS	Iso	Single	Constant	FDM	Grain
Wen and Wang	1970	PSS	Non	Single	$D \propto T$	Analytical	SCM
Wen and Wei	1970	PSS	Non	Multiple	$D \propto T$	Analytical	SCM
Sohn and Szekely	1972	PSS	Iso	Single	Constant	Numerical integration	SCM
Rehmat and Saxena	1978	PSS	Non	Single	$D \propto T$	Analytical	SCM
Tsay et al.	1976	PSS	Iso	Multiple	Constant	Analytical	SCM
Yu and Gillis	1981	PSS	Iso	Single	Constant	Numerical	Homogeneous
Johnson and Hindmarsh	1983	USS	Iso	Single	Stephen/Maxwell	FDM	Homogeneous
Usui et al.	1983	Both	Iso	Single	Constant	FDM/analytical	Zone
Hindmarsh and Johnson	1983	USS	Non	Multiple	Stephen/Maxwell	FDM	Homogeneous
Eddings and Sohn	1993	PSS	Iso	Multiple	Effective Maxwell	FDM	SCM
Patisson et al.	1998	USS	Non	Single	Stephen/Maxwell	FVM	Homogeneous
Patisson and Ablitzer	2000	PSS	Non	Single	Effective	FVM	Homogeneous
Patisson and Ablitzer	2000	USS	Non	Single	Effective	FVM	Homogeneous
Gupta and Saha	2004	PSS	Iso	Single	$D \propto T^{\beta}$	FVM	SIM
Gupta and Saha	2003	USS	Non	Both	$D \propto T^{\beta}$	FVM	SIM
Gupta and Saha	2003	USS	Iso	Single	$D \propto T^{\beta}$	FVM	Zone
Valipour et al.	2006	USS	Iso	Multiple	Effective	FVM	Grain

2.4 Simplifications of Chemical Complexities and Computational Effort

With reference to **Table 2.1**, mathematical modeling of gas-solid reaction with solid product and chemical complexities is normally very complicated and cannot be solved easily and accurately. It may also take very lengthy computational effort. Therefore, many researchers follow the approach of using relatively simple formulations to develop a kinetic model whose assumptions were made to simplify the equations. The most important simplifications that have been used in the literature can be classified into four main approximations which are Pseudo-steady state, isothermal condition, single reactant for gas and solid and simplification in physic-chemical properties.

2.4.1 Pseudo-Steady State Approximation

By taking the Pseudo-steady state approximation, the accumulation term in the gaseous phase is neglected and the governing equations are relatively simplified for analytical solution. This approximation has been extensively used in modeling work reported in the literature except for study in which a numerical method solution is required. Pseudo-steady state approximation has been shown to be valid for isothermal gas-solid reactions (Rehmat and Saxena, 1976). However this will cause significant error when this assumption is used in the case of non-isothermal models (Wen, 1968; Aris,1972; Georgakis and Aris, 1975; Heineken, 1967).