REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING CERIUM-MODIFIED PALM SHELL ACTIVATED CARBON

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by

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This thesis is especially dedicated to my beloved belated mother

DAMAYANTHI MUTHUVELU

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A	Coded variables for retention time of N_2 gas
A_o	Frequency or pre-exponential (min^{-1})
B	Coded variables for flow rate of N_2 gas
C	Coded variables for activation temperature
C_a	Initial concentration (ppm) of gas in the particular gas cylinder
C_b	Desired concentration (ppm) of gas from the particular gas cylinder
C_e	Equilibrium concentration of gas or breakthrough concentration (ppm or mg/l or $kmol/m^3$)
$C_{,i}$	Initial concentration of each component *i*
C_o	Initial concentration of gas (ppm or mg/l or $kmol/m^3$)
D	Coded variables for flow rate of CO_2 gas
E	Coded variables for retention time of CO_2 gas
E_a	Activation energy (kJ/mol)
F_s	Gas flow rate (ml/min) set by the mass flow controller
F_t	Total flow rate (150ml/min) of gases mixture
i	Linear interaction coefficients
j	Quadratic interaction coefficients
k	Proportionality constant
k_{ap}	Deactivation of apparent reaction rate constant
k_d	Deactivation rate constant (min^{-1})
K_F	Adsorption or distribution coefficient for Freundlich isotherm($mg/g(L/mg)^{1/n}$)
K_L	Langmuir constant related to rate of adsorption (l/mg)
$K_{L,i}$	Langmuir constants obtained from the corresponding single adsorbate sorption isotherm
k_o	Initial sorption rate constants (m^3/kg.min or cm^3/g.min)
K_{YN}	Rate constant (min^{-1})
m_c	Mass of adsorbent used inside the bed
n	Freundlich constant
N	Number of the components
n_{ij}	Correction parameter of species $_i$ and $_j$
p	Number experimental

Q_f	Volumetric flow rate (m^3/min)
q	Amount adsorbed per unit mass of adsorbent (mg/g)
$q_{,i}$	adsorption capacity of the component *i*
q_s	Langmuir constant related to adsorption capacity (mg/g)
$q_{o,i}$	Langmuir constants obtained from the corresponding single adsorbate sorption isotherm
R	Gas constant (8.314 J/mol·K)
R^2	Correlation Coefficient
r_i,	Residual value from the model
T	Solution temperature (°C or K)
t	Reaction time (min)
t_t	Time equivalent to the total or stoichiometric capacity
$t_{1/2}$	Time required for 50% sorbate breakthrough (min)
V	Volume of the gas mixture (l)
W	Mass of adsorbent used (g)
X	Coded value of variables
x_1	Coded term of activation temperature (°C)
x_2	Coded term of retention time of CO_2 gas (min)
x_3	Coded term of retention time of N_2 gas (min)
x_4	Coded term of flow rate of CO_2 gas (ml/min)
x_5	Coded term of flow rate of N_2 gas (ml/min)
x_{max}	Maximum values of the natural variables
x_{min}	Minimum values of the natural variables
y	Predicted responses
Y_1	Coded term of BET surface area (m^2/g)
Y_2	Coded term of Total pore volume (cc/g)
Y_3	Coded term of Micropore fraction (%)
Y_4	Coded term of Carbon yield (g)
y_f	Mole fraction of adsorbate in the feed
Y_i	Calculated value from the model
$y_{i,cal}$	Calculated responses
$y_{i,exp}$	Experimental responses
β	Offset term for regression coefficients

ΔG°	Free energy change (kJ/mol)
ΔH°	Enthalpy change (kJ/mol)
ΔS°	Entropy change (kJ/mol·K)

LIST OF ABBREVIATION

CO	Carbon Monoxide
NOx	Oxides of Nitrogen
SOx	Oxides of Sulfur
VOC	Volatile Organic Compounds
SO_2	Sulfur Dioxide
NO	Nitrogen Oxide
N_2	Nitrogen
O_2	Oxygen
RMG	Recommended Malaysian Air Quality Guidelines
API	Air Pollutant Index
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
AC	Activated Carbon
CO_2	Carbon Dioxide
De-NOx	Denitrification
De-SOx	Desulfurization
EFB	Empty Fruit Bunch
MF	Mesocarp Fiber
PS	Palm Shell
NO_2	Nitrogen Dioxide
NH_3	Ammonia
H_2S	Hydrogen Sulphide
FGD	Flue Gas Desulfurization
DOE	Design Of Experiments
PSAC	Palm Shell Activated Carbon
SV	Space Velocity
MEL	Modified Extended Langmuir
FBC	Fluidized-Bed Combustion
IGCC	Integrated Gasification Combined-Cycle
CCGT	Combined-Cycle Gas Turbines

ACF	Activated Carbon Fiber
EB	Electron Beam
FCC	Fluidized Catalytic Cracking
RSM	Response Surface Methodology
CCD	Central Composite Design
CCC	Central Composite Circumscribed
CCI	Central Composite Inscribed
CCF	Central Composite Faced Centered
AAD	Absolute Average Deviation
LOF	Lack of Fit
SST	Total Sum of Squares
SSE	Error of Sum of Squares
SS	Sum of Squares
DF	Degree of Freedom
MS	Mean Square
CV	Coefficient of Variation
SO	Standard Order
LPG	Liquefied Petroleum Gas
DR	Dubinin-Radushkevich
IAST	Ideal Adsorbed Solution Theory
BDST	Bed Depth Service Time Model
PSAC/Ni	Palm Shell Activated Carbon Impregnated With Nickel Oxide
PSAC/Ce	Palm Shell Activated Carbon Impregnated With Cerium Oxide
PSAC/Ce10	Palm Shell Activated Carbon Impregnated With 10wt% of Cerium Oxide
PSAC/V	Palm Shell Activated Carbon Impregnated With Vanadium Oxide
PSAC/Fe	Palm Shell Activated Carbon Impregnated With Ferum Oxide
ANOVA	Analysis of Variance
MFM	Mass Flow Meters
TGA	Thermogravimetric Analyzer
BET	(Brunauer-Emmett-Teller)
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray
TEM	Transmission Electron Microscope

FTIR	Fourier Tranform Infrared Spectroscopy
EA	Elemental Analyzer
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction

PENYINGKIRAN SO_2 DAN NO DARIPADA GAS SEROMBONG SELAKU MENGGUNAKAN SERIUM-TERUBAHSUAI KARBON TERAKTIF KELOMPANG KELAPA SAWIT

ABSTRAK

Fokus penyelidikan ini adalah mengkaji penggunaan karbon teraktif berasaskan kelompang kelapa sawit (PSAC) sebagai penyerap bagi penyingkiran serentak SO_2 dan NO dari gas serombong selaku. Industri minyak kelapa sawit memainkan peranan utama di dalam ekonomi Malaysia terutamanya dalam mempertingkatkan kebajikan ekonomi populasi negara. Walaupun pembangunan industri ini membawa manfaat yang jelas, kegiatannya mengakibatkan penghasilan sisa pepejal yang banyak. Salah satu sisa pepejal tersebut adalah kelompang kelapa sawit yang berasal daripada tandan buah kelapa sawit. Di dalam penyelidikan ini, kebolehlaksanaan untuk menukar kelompang kelapa sawit kepada karbon teraktif telah dikaji bersama dengan terbitan logam untuk penyingkiran gas SO_2 dan NO secara serentak. Produksi karbon teraktif dioptimasikan menggunakan reka bentuk eksperimen. Didapati bahawa model matematik yang dibangunkan dapat memberikan ramalan yang memuaskan bagi nilai mikroliang dan luas permukaan karbon teraktif kelompang kelapa sawit (PSAC) di dalam julat pembolehubah yang dikaji. Kondisi optimum operasi pengeluaran karbon teraktif kelompang kelapa sawit (PSAC) adalah masa penahanan gas N_2 dan CO_2 selama 50min dan 90min masing-masing, kadar aliran gas N_2 dan CO_2 sebanyak 500ml/min dan suhu operasi sebanyak 1090°C. Karbon teraktif yang disediakan potensinya dicuba untuk menyingkirkan SO_2 dan NO daripada gas serombong selaku. Karbon teraktif teroptimum yang dihasilkan hanya berupaya menyingkirkan gas SO_2. Muatan erapan masimum bagi gas SO_2 dan NO ialah 76.60mg/g and 0.72mg/g masing-masing. Oleh yang demikian, di dalam kajian ini bagi mempertingkatkan muatan erapan karbon teraktif kelompang kelapa sawit (PSAC), terbitan logam telah ditambah dengan menggunakan kaedah pengisitepuan. Nitrat logam seperti nikel, cerium, vanadium dan ferum telah digunakan. Didapati bahawa karbon teraktif kelompang kelapa sawit (PSAC) berisitepukan cerium menunjukkan penyingkiran NO yang baik berserta penyingkiran gas SO_2 dan NO secara serentak. Muatan Ce sebanyak 10% keatas PSAC memberikan muatan erapan sebanyak 121.72mg/g untuk SO_2 and 3.46mg/g untuk NO daripada per gram PSAC-Ce. Kondisi operasi yang optimum untuk muatan erapan ini adalah dengan alat penjerap pada suhu 150°C dan gas suapan yang mengandungi 2000ppm SO_2, 500ppm NO, 10% O_2, 15% kelembapan nisbi (RH) dan diseimbangan dengan N_2 kepada jumlah kadar aliran sebanyak 150ml/min. Satu analisis bulus yang lengkap mengenai keadaan operasi seperti suhu, halaju ruang, kelembapan, dan kepekatan suapan SO_2 dan NO telah dilakukan. Semua faktor ini mempengaruhi muatan erapan bagi SO_2 dan NO ke atas karbon teraktif kelompang kelapa sawit (PSAC) berisitepukan cerium. Satu kajian fana telah dikendalikan dengan memperkenalkan perubahan berlangkah dalam komposisi SO_2, NO dan O_2 pada karbon teraktif kelompang kelapa sawit (PSAC) dan karbon teraktif kelompang kelapa sawit (PSAC) berisitepukan cerium. Berdasarkan kajian ini, dapat disimpulkan bahawa NO boleh disingkirkan dengan mudah oleh kedua-dua jenis karbon teraktif, dengan syarat SO_2 tidak diperkenalkan ke dalam sistem itu. Ini adalah kerana SO_2 bertindak sebagai pesaing penyingkiran NO. Penyingkiran secara serentak ini juga dikaji berdasarkan model erapan individu dan perduaan. Ciri-ciri termodinamik telah dinilai dan satu model bulus telah disesuaikan untuk meramalkan lengkung bulus sistem ini. Tenaga pengaktifan untuk erapan SO_2 dan NO ialah 7.84 kJ/mol dan 19.66 kJ/mol masing-masing. Akhirnya, pelbagai jenis pencirian seperti TEM, SEM, EDX, luas permukaan BET, XRD, TGA, FTIR telah dijalankan untuk membuktikan data-data penyingkiran SO_2 dan NO menggunakan karbon teraktif kelompang kelapa sawit (PSAC) berisitepukan cerium.

REMOVAL OF SO_2 AND NO FROM SIMULATED FLUE GAS USING CERIUM-MODIFIED PALM SHELL ACTIVATED CARBON

ABSTRACT

The focus of this research was to study the usage of oil palm shell made activated carbon as a sorbent to remove SO_2 and NO gases simultaneously from simulated flue gas. The palm oil industry plays a major role in Malaysian economic especially in enhancing the economic welfare of the population. Despite obvious benefits of this industrial development, its activity contributes to abundant solid waste. Palm shell derived from the fruit bunch of oil palm, is one of the solid wastes. In this study, the conversion of oil palm shells into activated carbon followed by modification with metal derivatives was examined for simultaneous removal of SO_2 and NO. The production of palm shell activated carbon (PSAC) was optimized using design of experiment. It was found that the developed design predicted the micropores and surface area of PSAC satisfactorily within the range of the variables studied. The optimum operating condition for preparing the PSAC was 50min of N_2 and 90min of CO_2 retention time respectively, 500ml/min of N_2 and CO_2 flow rate and an operating temperature of 1090°C. The prepared activated carbon was tested for its potential of removing SO_2 and NO gases from simulated flue gas. The optimized PSAC could only remove SO_2 successfully. The maximum sorption capacity of SO_2 and NO was 76.60mg/g and 0.72mg/g respectively. Thus in this study, metal derivatives were added to enhance sorption capacity of the PSAC through impregnation method. Metal nitrates such as nickel, cerium, vanadium and ferum were used. It was found cerium impregnated PSAC shows good removal of NO as well as simultaneous removal of SO_2 and NO gas. A 10% loading of Ce onto PSAC resulted 121.72mg/g of SO_2 and 3.46mg/g of NO sorption capacity per gram of PSAC-Ce. The operating conditions for this optimized sorption capacity are an adsorber temperature of 150°C and feed gas containing 2000ppm SO_2, 500ppm NO, 10% of O_2, 15% of relative humidity (RH) and with N_2 balanced to a total gas flow rate of 150ml/min. A complete breakthrough analysis of operating conditions such as temperature, space velocity, humidity, and feed concentration of SO_2 and NO was done. All these factors were influencing the sorption capacity of SO_2 and NO onto PSAC impregnated with cerium (PSAC-Ce). A transient study was conducted by introducing stepwise changes to the composition of SO_2, NO and O_2 on PSAC and PSAC-Ce. Based on this study it was concluded that NO can be removed easily by PSAC or PSAC-Ce, provided SO_2 was not introduced into the system because SO_2 acts as a competitor to NO removal. The simultaneous removal was also analyzed based on single and binary sorption models. Thermodynamic properties were evaluated and a breakthrough model was fitted to this system to predict the breakthrough curves. The activation energy for SO_2 and NO sorption were 7.84 kJ/mol and 19.66 kJ/mol respectively. Finally various types of characterization such as TEM, SEM, EDX, BET surface area, XRD, TGA, FTIR were done to prove the data of SO_2 and NO removal using PSAC impregnated with cerium.

CHAPTER 1

INTRODUCTION

1.1 Air Pollution

Air pollution worldwide is a growing threat to human health and the natural environment. The acidification of land and water through air pollution has received more and more attention in recent years, especially in the developing third world nations alike Asia. It is claimed that the mounting numbers of damage to human health, the damage of forests, global warming and extreme climate change, can be attributed to the re-deposition of man-made acid gases. Fuel combustion is the largest contributor to air pollutant emissions, caused by man, with stationary and mobile sources are equally responsible. The most widespread pollutants which are called the primary pollutants include carbon monoxide (CO), oxides of nitrogen (NOx), oxides of sulfur (SOx), volatile organic compounds (VOC), hydrocarbons, metals and particulate matter (Kiely, 1997 & Schnelle & Brown, 2002).

The acid gases of concern are the sulfur dioxide (SO_2) and NOx from power plants, petrochemical plants and smelting factories. SO_2 is formed from the oxidation of sulfur contained fossil fuels and industrial processes that treat and produce sulfur-containing compounds (Schnelle & Brown, 2002). Whereas NOx is a principal by-product of combustion processes, arising from the high temperature reaction between N_2 and O_2 in the combustion air (Jaime, 1993). The contribution of the latter is comparatively small on a regional basis but the emission rate is high, and thus significant with respect to local ambient air quality.

In Malaysia, the goal of achieving industrial country status by the year 2020 and the associated rapid economic growth have started to impose costs in terms of industrial pollution and the degradation of urban environment. Among them, air pollution is the major issue. Studies on the ambient air quality show that air pollutants in several large cities are increasing with time and are not at par with the acceptable levels. It is estimated that in year 2007 the combined air pollutant emission load was about 2,534,447 metric tones. A comparison of the combined air pollutant emission load in 2006 and 2007 is shown in Fig.1.1 (Malaysia Environmental Quality Report, 2007).

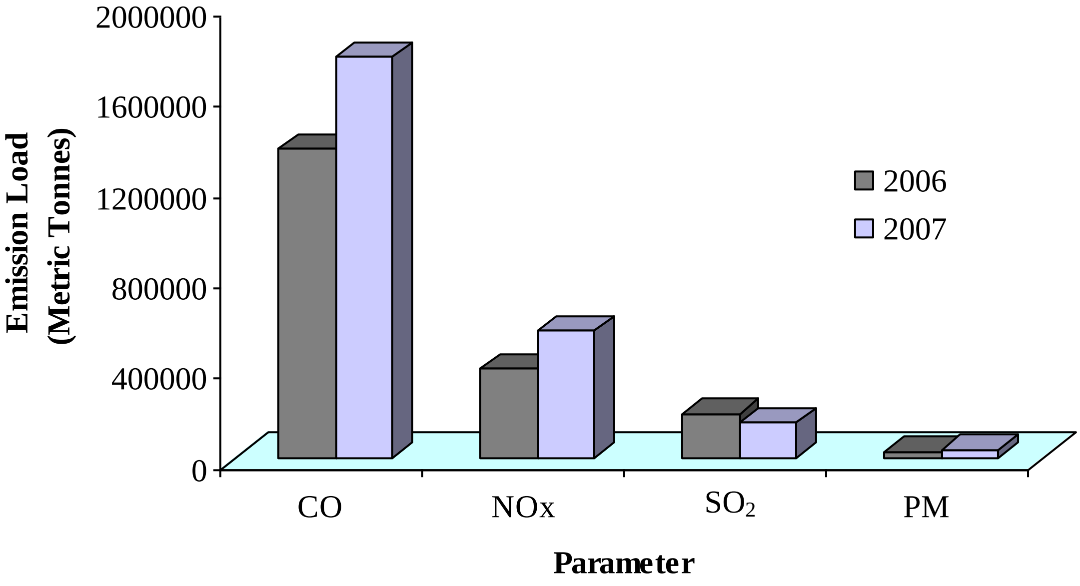

Fig. 1.1 Air pollutant emission load from all sources in Malaysia, 2006-2007

Three major sources of air pollution in Malaysia are mobiles, industries and power stations. Table 1.1 shows the various pollutants and their source for Malaysia adopted from Country Synthesis Report on Urban Air Quality Management, Malaysia, 2006 (Legal Research Board Malaysia, 2006) and Malaysia Environmental Quality Report, 2007.

Table 1.1 Emissions inventories of SO_2 and NOx by sources in 2006 and 2007

Sources	**Percentage (%)**			
	SO_2		**NOx**	
	2006	**2007**	**2006**	**2007**
Transportation	5	16	58	70
Power stations	60	41	7	16
Industries	23	23	31	12
Others such as domestic furnaces, commercial furnaces and open burning	12	20	4	2

Furthermore, it is estimated that the total health damage costs were estimated to be RM 129 million, with a lower estimation of RM 36 million and a higher estimation of RM 258 million per annum (Afroz *et al.*, 2003). Owing to such a hazardous condition, health damages and the limitation of releasing these dangerous gases to the open air, it is therefore imperative for the emission rate to be reduced or controlled to meet the Malaysian guidelines. There are a set of specified limitation for SO_2 and NOx gases in Malaysia. The government has set air quality standards & guidelines, termed Recommended Malaysian Air Quality Guidelines (RMG) for air pollutants, defining the concentration limits of selected air pollutants which fight adversely on the health and welfare of the general public (Laws of Malaysia, 2005).

Department of Environment, Malaysia has revised its index system in 1996, and another type of index system Air Pollutant Index (API) was adopted. Table 1.2 shows the index limitation standards for SO_2 and NOx (Laws of Malaysia, 2005). With this guideline, it is evident that the authorities are taking a pro-active role in controlling and reducing the air pollution. This is done in order to maintain Malaysia as a balance country between the sustainability of industrial development and environmental care within the economic limitations.

Table 1.2 Recommended Malaysia Air Quality Limit Guidelines (At 25°C and 101.13kPa)

Pollutant & Method	Averaging Time	Malaysia Guidelines	
		ppm	µg/m^3
NO_2 AS 2447	1 Hour	0.17	320
	24 Hour	0.04	10
SO_2 AS 2523	10 minutes	0.19	500
	1 Hour	0.13	350
	24 Hour	0.04	105

1.2 Control Technologies

There are a number of technologies available in the market to remove the pollutant gases. The most common ones for SO_2 gas removal are wet and dry scrubber flue gas desulfurization whereas for NOx removal are low burners, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). The present work is limited to the development of scrubbing processes only because it is much cheaper, more convenient and widely used in the industries. From the literature review presented in Chapter 2, there are three types of scrubber utilized in curbing flue gas such as the wet, semi-dry and the dry processes. Dry scrubbing was found to be very promising with respect to its simplicity, cost effectiveness and ability to accomplish SO_2 and NOx removal (Chu *et al.*, 2000; Sakai *et al.*, 2002; Lee *et al.*, 2005; 2006) simultaneously.

As reported by many researchers (Juntgen, 1986; Dąbrowski *et al.*, 2005; Chun *et al.*, 2007; Gianluca *et al.*, 2008), activated carbon (AC) is a common type of material currently being applied in many industries as adsorbents, catalyst supports and separation media. AC possesses an adsorption capacity for various types of noxious gases such as SOx, VOC, carbon dioxide (CO_2) and CO. AC also has a catalytic activity for NOx reduction and high mechanical strength to resist abrasion and crushing (Kazuhiko & Ikuo, 1997).

AC's are used because of its large adsorption capacity, well-developed porous structure, large surface area, fast adsorption kinetics and relative ease of regeneration. Furthermore AC's can adsorb organic and other non-polar compounds from liquid and gaseous phases (Zhonghua and Srinivasan, 1999). Due to this universality, AC is now finding wider application in Asia and paving its way in Malaysia. Nowadays, AC can be produced from a large number of abundant and low-cost materials, which possess high carbon content and a low inorganic content (Olivares-Marin *et al.*, 2006).

1.3 Biomass Activated Carbon

Carbon based flue gas desulfurization systems have achieved commercial success and can remove up to 100% of the SO_2 from combustion flue gas streams (Carabiniero *et al.*, 2003). Therefore various kinds of AC's prepared from various carbonaceous materials have been used to remove NOx and SOx gases. Waste biomass can be also used to produce AC. Over the last decade or so, increasing attention is now focused on the use of carbonaceous agricultural solid residues such as coconut shell, palm shell (PS), rice husk, corn cobs, olive, prunes, sunflower straw, corn stalks, sugar beet leaves and many others as starting materials due to their low cost, renewable sources and its potential of producing good quality AC (Ioannidou and Zabaniotou, 2007; Suhas *et al.*, 2007).

Among them, coconut shell is one of the most widely used biomass to produce AC. Literatures show that it has been applied in the current existing combustion processes for denitrification (De-NOx) and desulfurization (De-SOx) (detailed literature in Chapter 2). Recently, PS has been reported as a new promising biomass to produce AC with high surface area and predominant microporosities which can be used for gas phase applications (Lua & Guo, 2001a;b).

1.4 Malaysian Palm Shell Activated Carbon

Malaysia is currently the world's largest producer and exporter of palm oil. Malaysia produces about 47% of the world's supply of palm oil. Besides producing oils and fats at present there is a continuous increasing interest concerning renewable energy from waste biomasses. In Malaysia, agricultural by-products are the most abundant biomass resources, exceeding 70 million tonnes annually (MPOB, 2009).

Palm oil industry is the main contributor of agricultural biomass, generating 94% of the total agricultural biomass. Huge quantities of biomass by-products are used to produce value added products such as methane gas, bio-plastic, organic acids, bio-compost, ply-wood, AC and animal feedstock (MPOC, 2009). Table 1.3 shows types of biomass produced from oil palm tree and the quantities produced per annum in million tonnes.

Table 1.3 Types of biomass and quantity produced (MPOB, 2009)

Type of Biomass	Quantity Per Annum (MnT)
Empty Fruit Bunch (EFB)	15.8
Fronds	12.9
Mesocarp Fiber (MF)	9.6
Trunk	8.2
Palm shell (PS)	4.7

These biomasses have high potential of turning into renewable energy. Attempts have been made to convert these bio-products into chemicals and other value added products such as pulp and paper, particle boards, pelleted fuels, soil conditioners and as a source of fertilizer (MPOC, 2009).

The latest research and output of the local scientists proved that these palm kernels, empty fruit bunch (EFB), PSs and stones can be also converted into AC (Gua & Lua, 2000; Lua & Gua, 2001; Gua & Lua, 2002a). The potential of PS as a good precursor of AC may be seen by comparing the ultimate analysis of other more established biomasses such as wood, nut shells, straws and fruit stones. The details of the ultimate analysis can be referred in Chapter 2. PS has high oxygen and carbon content, this characteristic are known to produce microporous AC (Muhlen & Van Heek, 1995), which is suitable for gas phase applications.

The earliest investigation into the possible production of the AC and the distillation of other volatiles from the PS were developed by Chan *et al.* (1976). The volatiles by-products include creosote (11%), phenols (2.5%), methanol (0.4%), acetic acid (5.2%) and other gases (17%). AC yield reported by them were 17%. The report even concluded that even if 70% of the PS are burnt as cheap fuel in boilers, a considerable quantity would still be available for carbonization and for extraction of other products of economic value. Current researchers have reported a higher yield of AC by optimizing the production parameters and also using different types of precursors such as KOH, H_3PO_4 and $ZnCl_2$. A yield of 30% and above has been reported by Gua & Lua (2000a).

Oil palm activated carbon has been used to treat air toxics such as CO, nitrogen dioxide (NO_2), ammonia (NH_3) and SOx (Gua & Lua, 2002b; Lua *et al.*,

2006) but then none have been reported on NOx and simultaneous removal of SO_2 and NOx. Gua *et al.* (2007) have used PS to adsorb hydrogen sulphide (H_2S).

1.5 Problem Statement

In Malaysia, lately the emissions of SO_2 and NOx gas from various sources of combustion have caused human health and environmental problem. Thus, efforts to control these SO_2 and NOx emissions has become a great deal to the Department of Environment, Malaysia as well as to the general public. There are many existing technologies to abate this problem such as wet-method of flue gas desulfurization (FGD) technology based on limestone, lime or sodium carbonate. This process is known to remove SO_2 efficiently however it could not remove NOx. Hence, another separate process is considered to remove NOx mainly through modification of the combustion process itself or post-treatment via selective catalytic or non-catalytic reduction. The need of two separate systems to remove SO_2 and NOx are very expensive and not advisable for small scale industries. Lately dry-methods have been used to remove SO_2 and NOx simultaneously but then the sorption capacities are much lower comparatively to wet-methods. Thus it has been a great task to enhance the sorption capacities of dry sorbents.

Currently in Malaysia there is an urgent requirement to develop a cheap local technology to reduce these acidic gases from local industries. Furthermore there is also a demand from Malaysian palm oil mills to find new applications for waste by-products and the possibility of generating value added product to the waste materials. In order to manage the requirements and demands, this research study can be materialized with a process which simultaneously remove SO_2 and NOx at an economical cost and concurrently exploit the usage of palm oil mill waste by-products.

Hence this thesis will cover the development of AC from PS to treat flue gas. The scope is limited to SO_2 and NOx /flue gas treatment in order to evaluate the potential of Malaysian biomass by-product utilization.

1.6 Research Objective

The main objective of this research study is to develop a technology for simultaneous removal of SO_2 and NO utilizing activated carbon (AC) synthesized from palm shell (PS). The following are the measurable objectives of this research work.

1. To produce, characterize and analyze the PS made AC for the removal of SO_2 and NO gas from stimulated flue gas.
2. To study the impregnation of metal oxides onto PSAC for the removal of SO_2 and NO and infer the optimum operating parameters.
3. To study the sorption behavior of SO_2 and NO in the presence and absence of O_2 as a transient study.
4. To study the effect of various operating parameters affecting the simultaneous removal of $SO_2$and NO using the optimum PSAC.
5. To study the sorption equilibria, isotherms, reaction rate thermodynamics and breakthrough model for the simultaneous sorption of $SO_2$and NO over PSAC.

1.7 Scope of Study

In this study, the term sorption (by sorbent) was used to represent surface phenomena which maybe either absorption of adsorption, or a combination of them. In the current study, only SO_2 and NO gases are focused and used in the mixture of the simulated flue gas as both these gases are the major components emitted by combustion processes. As mentioned earlier in section 1.3, PS has been reported as a new promising biomass to produce AC which could be used for flue gas cleaning. Thus in this study the preparation of AC from PS and its potential usage as a sorbent to remove SO_2 and NO were analyzed. Since there are many variables affecting the carbonization and activation of AC preparation, however, this study focused only on the effect of five variables (flow rate of N_2 and CO_2, retention time of N_2 and CO_2 and operating temperature). These variables are carefully selected based on literature and some preliminary experiments. In this preparation steps, design of experiments (DOE) was used to study the effect of AC preparation variables in order to ease the conventional laboratorius and time-consuming work load. DOE also help to develop a mathematical model for the optimized preparation variables.

Once the PSAC is prepared it was analyzed for SO_2 and NO. Simulated flue gas containing 2000ppm of SO_2, 500ppm of NO, 10% of O_2 and N_2 as the balance with a total flow rate of 150ml/min, was used to study the performance of the prepared PSAC. Water vapor in term of (%) relative humidity (RH) was only applied in the later stage as process study. Depending on the results, PSAC was then incorporated with selected metal oxides to enhance the simultaneous removal of SO_2 and NO. Once the specified PSAC sorbent obtained under optimum condition for maximum simultaneous removal of SO_2 and NO was found, a process study was done. This was done by varying the operating conditions of the adsorber *i.e.*, feed concentration of SO_2 and NO (ppm), operating adsorber temperature (°C), space velocity (SV) and (%) RH.

The amount of SO_2/NO captured by PSAC sorbent was recorded continuously until it shows negligible activity/saturation (the outlet concentration of SO_2/NO becomes the same as the inlet concentration). The removal activity of the prepared PSAC sorbent towards SO_2/NO was expressed in two terms *i.e.* sorption capacity and breakthrough curve. The sorption capacity was expressed by the weight of SO_2/NO captured per gram of PSAC sorbent from the simulated flue gas. Breakthrough curves were also used to report the sorption activity of PSAC sorbent.

The reaction between the prepared and optimized PSAC sorbent and SO_2/NO was complicated, thus a transient study was done in order to understand the reactions between the gaseous mixture and PSAC sorbent. Adsorption isotherm equations *i.e.* Langmuir and Modified Extended Langmuir (MEL) were used to describe single and binary mixtures of SO_2 and NO. Deactivation kinetic model was used to predict the thermodynamics properties and breakthrough curve of PSAC sorbent.

Besides, the theoretical breakthrough curves at different equilibrium temperatures are generated and compared with corresponding experimental data using Yoon and Nelson model (1984). This model gives an equation predicting the whole breakthrough curve for the simultaneous sorption of SO_2 and NO by PSAC sorbent.

1.8 Organization of Thesis

This thesis consists of five chapters. Chapter 1 (introduction) present a brief idea of the harmful effect of air pollution towards the world and community, especially SO_2 and NO gases. Current scenario of air pollution problem in Malaysia and various control strategies to solve this problem were also discussed. The use of biomass made AC in current existing combustion processes is particularly promising. On the other hand, new applications of PS derived AC was exploited. Therefore this introduction section tries to match their mutual needs and thus justify the present work.

Chapter 2 (Literature Review) is an extensive literature search. Literature search has been conducted, especially on the areas affecting most of the main task of the present research, namely desulfurization and denitrification technology, various types of sorbents in diverse conditions used for SO_2 and NO removal, a brief revive of AC, experimental design, method and concept and fundamental concept of the transient kinetic model. Other topics have been surveyed briefly but precisely in order to cover the overall aspects of the thesis.

In Chapter 3 (Materials and Methods) the details of all material and chemicals used in the present study was listed. This chapter begins with a schematic flow diagram, showing the overall experimental activities carried throughout this research. This is followed by descriptions on the experimental rigs and schematic diagrams. Methods of AC production from PS, characterizations procedures and sorbent preparation were described. Subsequently, procedures used for sorbent sorption studies, data collection and observations were depicted. The experimental tool used, *i.e.* statistical DOE are elaborated in detail in this section. Finally the methods applied to study the sorption isotherm, kinetic and thermodynamic were described.

Chapter 4 (Results and Discussion) is the core of this thesis. This chapter presents the results of PSAC and PSAC impregnated with metal based sorbent preparation. The optimized results based on sorption capacity were discussed. An attempt to optimize the preparation variables was carried out using statistical DOE. The prepared PSAC was then analyzed on simultaneous removal of SO_2 and NO and the out comes were reported accordingly in this chapter. The effect of various operating conditions on sorption studies were conducted and analyzed. In the last section the sorption equilibria, kinetics, thermodynamics and breakthrough model of PSAC on SO_2 and NO sorption were presented.

Finally conclusion for the findings of this research is drawn in Chapter 5 (Conclusions and Recommendations) and as usual suggestions for future research are listed to enlarge the scope as well as deepen the various areas of concern.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The following survey covers the desulfurization and denitrification technology including: the interaction of SO_2 and NO_x with various types of sorbents in diverse conditions, simultaneous removal of SO_2 and NO_x, application and demand of activated carbon (AC), AC production, experimental design, method and concept for AC production and finally the fundamental of adsorption isotherm, thermodynamics, sorption rate and breakthrough model for the simultaneous removal. The objective is to consign the knowledge in the area in which the present research lies on a good and sound foundation.

2.2 Desulfurization (De-SOx) Technology

Sulfur present in fossil fuels, such as oil and coal. Fossil fuel combustion processes are the main source of anthropogenic SO_2 emissions from stationary sources. The sulfur is oxidized during combustion, and from there sulfur dioxide (SO_2) is formed. In addition, some non-combustion processes may contribute considerably to the emissions. The major stationary source categories include (Noel, 2000):

- Public power, cogeneration and district heating plants:

    (a)Boilers;

    (b) Stationary combustion turbines and internal combustion engines;

- Commercial, institutional and residential combustion plants:
  (a) Commercial boilers;
  (b) Domestic heaters;
- Industrial combustion plants and processes with combustion:
  (a) Boilers and process heaters;
  (b) Processes, e.g. metallurgical operations such as roasting and sintering, coke oven plants, processing of titanium dioxide (TiO_2), etc.;
  (c) Pulp production;
- Non-combustion processes, e.g. sulfuric acid production, specific organic synthesis processes, treatment of metallic surfaces;
- Extraction, processing and distribution of fossil fuels;
- Waste treatment and disposal, e.g. thermal treatment of municipal and industrial waste.

The power plant sector in many countries is the major single contributor to SO_2 emissions. In some countries, the industrial sector (including refineries) is also an important SO_2 emitter. Typically 60% of the SO_2 intake present in the crudes and the remains in the products. The 40% in the products was recovered as elemental sulfur (30%) and the rest (10%) was emitted through the refinery stacks (UNECE, 2008). Hence to avoid the subsequent oxidation of SO_2 to SO_3 followed by reaction with water vapor to form H_2SO_4 (acid rain), the flue gas has to be cleaned. There are two general options for reduction of SO_2 emissions *i.e.* energy management measures and technological management.

Energy management is done by energy saving and mix, whereby the rational use of energy (improved energy efficiency/process operation, cogeneration and/or demand-side management) usually results in a reduction in SO_2 emissions. For energy mix, in general, SO_2 emissions can be reduced by increasing the proportion of non-combustion energy sources (*i.e.* hydro, nuclear, wind, etc.) to the energy mix. However, further environmental impacts have to be considered.

Currently there are four options of technology management which can be applied to reduce or control the SO_2 emissions. The options are fuel switching, fuel cleaning, advanced combustion technologies and flue gas desulfurization.

2.2.1 Fuel Switching

Fuel switching means changing the fuel used from high- to low-sulfur coals and/or liquid fuels or from coal to gas which leads to lower SO_2 emissions, but there may be certain restrictions, such as the availability of low-sulfur fuels and the adaptability of existing combustion systems to different fuels. The contents of sulfur in coal can range from 0.5% to 5% (EIA, 2009). Some coal or oil combustion plants are being replaced by gas-fired combustion plants (Per & Christer, 2004).

2.2.2 Fuel Cleaning

Cleaning of process gas (acid refinery gas, coke oven gas, biogas, etc.) is a state-of-the-art technology. Thus cleaning of natural gas is widely applied for operational reasons. Fuel cleaning is done by desulfurization of liquid fuels (light and middle fractions) or heavy fractions of crude oil. Desulfurization of atmospheric residue (bottom products from atmospheric crude distillation units) for the production of low-sulfur fuel oil is not, however, commonly practiced;

processing low-sulfur crude is usually preferable. Hydro-cracking and full conversion technologies have matured and combine high SO_2 retention with improved yield of light products. For this type of refinery, energy consumption and investment costs are increased. Current technologies to clean hard coal can remove approximately 50 per cent of the inorganic sulfur (depending on coal properties) but none of the organic sulfur. Thus the efficiency of SO_2 removal by coal cleaning is limited compared to flue gas desulfurization (Per & Christer, 2004; UNECE, 2009).

2.2.3 Advance Combustion Technologies

For the past 10 years, advanced combustion technologies with improved thermal efficiency are utilized to reduce SO_2 emissions e.g. fluidized-bed combustion (FBC): bubbling (BFBC), circulating (CFBC) and pressurized (PFBC); integrated gasification combined-cycle (IGCC); and combined-cycle gas turbines (CCGT) (Ayala & Venkataramani 1998). FBC is a combustion technology for burning hard coal and brown coal, but it can also burn other solid fuels such as petroleum coke and low-grade fuels such as waste, peat and wood.

Emissions can additionally be reduced by integrated combustion control in the system due to the addition of lime/limestone to the bed material (Ayala & Venkataramani 1998). By-products from this process may cause problems with respect to use and/or disposal, and further development is required. IGCC and CCGT also have been tried by many researchers such Droog *et al.* (1993), Rath *et al.* (1994) and Gupta *et al.* (1996). The IGCC process includes coal gasification and combined-cycle power generation in a gas and steam turbine. The gasified coal is burnt in the combustion chamber of the gas turbine. SO_2 emission control is achieved by the use of state-of-the-art technology for raw gas cleaning facilities upstream of the gas turbine. The technology also exists for heavy oil residues and bitumen emulsions.

2.2.4 Flue Gas Desulfurization (FGD) Processes

FGD processes are one of the most extensively used processes to control SO_2 emissions. In the past 15 years, FGD technology has made considerable progress in terms of efficiency, reliability (defined here as FGD operating hours divided by the boiler operating hours in a given period) and costs (Soud, 2000). These processes aim at removing already formed SO_2, and are also referred to as secondary measures. Presently, there are several common ways of reducing SO_2 emissions e.g. wet, semi-dry and dry processes.

Wet scrubbers, especially the limestone-gypsum process, are the front-running FGD technologies because of its high efficiency and reliability, limestone–gypsum wet flue gas desulfurization technology is the most commonly used technology for controlling the emission of SO_2 (Nygaard *et al.*, 2004). There are four main types of wet scrubbers, the spray scrubber, the packed tower, the jet bubbling reactor , and the double-loop reactor (Takeshita & Soud, 1993). The most common wet scrubber is the countercurrent spray scrubber on the bottom of which a holding tank for limestone dissolution, sulphite oxidation and crystallization of the solid byproduct is present (Kiil *et al.*, 1998). However, Miller (1986) had commented that this kind of technology generates a large amount of wet solid waste and requires treatment of waste water. It also involves a complicated configuration and costly operation.

Semidry FGD processes have been developed and adopted commercially since the 1980s. The spray dry scrubber process, as a typical semidry FGD process, is effective in removing SO_2 from flue gas and has been developed as an alternative to wet scrubbers (IEA Coal Research, 1997) and have the second largest market share following wet scrubbers (Ma *et al.*, 2000). However, according to Soud (1995), for achieving an SO_2 removal of greater than 95%, the ratio of sorbent to SO_2 must be approximately 2.0, which is much larger than that in wet scrubbers. Furthermore spray dry scrubbers produce the dry byproduct of calcium sulfite/sulfate and un-reacted reagent, which is less attractive commercially than the gypsum produced by the wet lime/limestone scrubber. Hence a widespread commercialization of semidry FGD process depends on further improving SO_2 removal efficiency, lowering operating cost and developing industrial application for their residues. Thus to overcome this problem new types of semidry FGD have been proposed by researchers *e.g* circulating dry scrubbing FGD (Neathery, 1996; Hou *et al.*, 2005) and powder particle spouted bag FGD (Xu *et al.*, 2000; Ma *et al.*, 2001).

According to Jianrong *et al.* (2003), although the once-through non-regenerative wet and semi-dry FGD processes, based mainly on limestone scrubbing are commonly used, dry and re-generable FGD technologies are expected to be increasingly preferred, because it offers a number of advantages; (1) a small sorbent make-up, (2) generation of relatively small amounts of by-products, (3) recovery of sulfur as useful-containing products, (4) simultaneous removal of SO_2 and NOx, (5) elimination of stack gas reheating and large water consumption.

Dry FGD is a process in which the SO_2 is removed from the gas stream by reaction with a dry material. Table 2.1 shows an overall review of the types of sorbent and materials used for dry FGD.

Table 2.1 Classification of sorbent and material for dry FGD

Types of Sorbent	Material	Reference
Calcium based	Lime (CaO)	Dasgupta *et al.*, 2003
	Hydrated Lime ($Ca(OH)_2$)	Mohamed *et al.*,2005;2006
	Lime stone ($CaCO_3$)	Chu *et al.*, 2000
	Calcium & Silica	Fernandez *et al.*,2001
		Ishizuka *et al.*, 2000
		Han *et al.*, 2005
		Lee *et al.*, 2005
		Liu & Shih 2006
		Krammer *et al.*, 2002
		Dahlan *et al.*, 2008a;b
Sodium based	Sodium carbonate (Na_2CO_3)	Keener & Khang, 1993
	Sodium bicarbonate ($NaHCO_3$)	Zhao *et al.*, 2002
	Trona ($NaHCO_3.Na_2.CO_3.2H_2O$)	Wu *et al.*, 2004
		Srinivasa, 2003
		Cho 2007
Activated carbon	The details will be listed in section	2.5.4
Metal oxides and mixed metal oxides	Al, Bi, Co, Ce, Co, Cr, Cu, Fe, Hf, Ni, Sn, Th, Ti, V, U, Zn, Zr	Lowell *et al.*, 1971
		Gavaskar, 2006
		Lee *et al.*, 2008
		Waqif *et al.*, 1997
		Fen *et al.*, 2007
		Rodas-Grapain *et al.*, 2005
Zeolites	Zeolite X	Srinivasan & Grutzeck, 1999
	Zeolite Y	Gupta *et al.*, 2004
	Zeolite Na-P1	Marcu & Sandulescu, 2004
	Type 5A	
Silica based	Coal fly ash	Lee *et al.*, 2006
	Quartz silica	Lin *et al.*, 2003
	Silica fume	Jung *et al.*, 2000
	Iron blast furnace slag	Liu & Shih, 2004
	Oil palm ash	Zainuddin *et al.*, 2005
	Coal fly ash	Mohamed *et al.*, 2005; 2006
	Rice husk	Dahlan, 2008

Basically from Table 2.1 it can be seen that for dry FGD processes, calcium and silica based sorbents are more favored. The researchers tested and investigated the usage of these calcium and silica based sorbents in many reactors such as bubbling fluidized bed (Chu *et al.*, 2000) and fixed bed (Mohamed *et al.*, 2005; Krammer *et al.*, 2002). In most of the studies it was found that humidity and temperature played an important role in desulfurization. Sodium based methods are also reported to be good on desulfurization. Cho (2007) studied a method of converting Na_2CO_3 fraction of parent trona ($Na_2CO_3.NaHCO_3.H_2O$) to $NaHCO_3$ to achieve more efficient removal of SO_2 in dry injection system.

The usage of metal oxides and mixed metal oxides has been reported as early as year 1971 by Lowell *et al.* (1971). After the pioneer work many researchers as listed in Table 2.1 have successfully used the metals to remove SO_2. In most recent work reported by Fen *et al.* (2007) Ceria doped with nanosized ZnO showed excellent removal of SO_2 by producing ZnS.

Zeolites are well known for dry type regenerative FGD process. Marcu & Sandulescu (2004) reported that Y type zeolite possesses good SO_2 sorption capacity. Many others as listed in Table 2.1 has also proven that Zeolite to be a good SO_2 remover.

Low cost sorbents as listed in Table 2.1 under silica base has been investigated as a replacement for currently available sorbent for removing SO_2. However most of the sorbents need to be activated prior to usage for optimum results. In more recent study the usage of oil palm ash and rice husk (Zainuddin *et al.*, 2005; Mohamed *et al.*, 2006; Dahlan *et al.*, 2008a;b) has been found to be successful for SO_2 removal.

A considerable amount of development effort has been aimed at dry sorption processes primarily because of their apparent advantage over aqueous absorption systems of permitting stack gas treatment without cooling and saturating the gas with water vapor. Several of the processes involve injection of the dry sorbents into existing boiler plant equipment or ductwork, resulting in a further potential advantage of low capital cost (Arthur &Richard, 1997).

2.3 Denitrification (De-NOx) Technology

Nitrogen oxides (NOx), is generally referred to nitrogen oxide (NO) and nitrogen dioxide (NO_2). They are generated primarily from combustion processes in the power stations and various vehicles. NOx emissions are formed in one of three ways *i.e.* thermal, fuel and prompt. Thermal NOx is produced when nitrogen and oxygen in the combustion air supply combine at high flame temperatures. Thermal NOx is generally produced during the combustion of both gases and fuel oils. Fuel NOx is produced when nitrogen in the fuel combines with the excess oxygen in the combustion air and is only a problem with fuel oils containing fuel bound nitrogen. Prompt NOx is formed during the early, low temperature states of combustion and is insignificant (Bacharach, 2010). For coal-fired units, thermal NOx generally represents about 25% and fuel NOx about 75% of the total NOx formed (Janssen & Meijer, 1993).

Other large sources of nitrous oxide emissions to the atmosphere are the soils of some forests, oceans, biomass burning, and fertilization. In the atmosphere, N_2O acts as a greenhouse gas as do carbon dioxide, methane, and water vapor. NO converts to NO_2, a yellowish-brown gas, in the atmosphere and in the presence of light. Man-made NOx emissions are produced from both mobile and stationary sources. Stationary sources, which account for approximately 53% of total NO emissions, can be broken down as follows (Arthur & Richard, 1997):

• Power Stations	53%
• Internal Combustion Engines	20%
• Industrial Boilers	14%
• Process Heaters	5%

- Combustion Turbines	2%
- Other	6%

The direct health effects of excessive NO_2 concentrations in the air include bronchitis and pneumonia. The emission of NOx into air are directly responsible to various environment problems, such as photochemical smog, formation of acid rain and resultant acidification of soils and waters, which has harmed some plants, animals and the human health (McMichael *et al.*, 2003). For these reasons, NOx emissions from the combustion processes are required to be severely controlled and regulated. Therefore, the abatement of NOx emission, *i.e.* De-NOx or denitrification, has attracted much attention and great efforts of worldwide researchers. Many NOx-controlling technologies have been developed. Currently, the removal of NOx from mobile sources that use gasoline uses the three-way catalyst whereas for stationary combustion sources it can be conveniently divided into three main categories, pre-combustion, combustion and post-combustion. In this research study the post-combustion De-NO processes are further reviewed. Post-combustion NO control processes can be classified as; selective non-catalytic reduction (SNCR), selective catalytic reduction (SCR), combined NO_x/SO_2 processes and NO_x adsorption processes.

2.3.1 Selective Catalytic Reduction (SCR)

SCR of NOx is believed to be one of the most promising ways, and has been one of the key subjects for research in heterogeneous catalysis (Janssen, 1997). SCR indicates, the selective conversion of nitrogen oxides (NO, NO_2 or N_2O) to nitrogen (N_2) in the presence of gaseous oxygen and a reducing agent, either inorganic (ammonia principally) or organic (saturated or unsaturated hydrocarbons (HC), oxygenated HC's such as methanol or nitrogen-containing chemicals such as urea). The SCR reactions, irrespective of the nature of the reductants, can be expressed as (Hu *et al.*, 2009);

$$NO_{(ads)} \rightarrow N_{(ads)} + O_{(ads)}, N_{(ads)} + O_{(ads)}, N_{(ads)} \rightarrow N_2 \qquad (2.1)$$

i.e., the mechanism of NO dissociation and subsequent O removal by reductant.

$$NO(ads) + R(ads) \rightarrow N \cdot\cdot O \cdot\cdot R(ads), N \cdot\cdot O \cdot\cdot R(ads) \rightarrow N_2 + O \cdot\cdot R(ads) \qquad (2.2)$$

i.e. the mechanism of forming intermediate species. Here, R represents reductant molecule; the intermediate can also be cyanide or isocyanate.

Nowadays, the large majority of the current industrial De-NOxing is carried out by this technology and ammonia is injected in the waste gases as the reducing agent. The industrial catalysts for the SCR process are based on TiO_2-supported V_2O_5-WO_3 and/or V_2O_5-MoO_3 oxides (Vogt *et al.*, 1991; Alemany *et al.*, 1996). Besides that metal oxides such as pure vanadia and vanadia supported on oxide carriers such as alumina, silica, zirconia and titania (which is the choice support nowadays) have been intensely investigated (Busca *et al.*, 1998).

Furthermore, catalysts based on pure, supported and/or mixed (e.g., Al_2O_3, TiO_2, ZrO_2, MgO, and these oxides promoted by, e.g., Co, Ni, Cu, Fe, Sn, Ga, In, Ag compounds) have also been proposed as supports and underwent wide application and testing in the literature (Busca *et al.*, 1998; Burch *et al.*, 2002). Transition metals have been also introduced into zeolitic cavities, such as in the cases of X, Y and ZSM5 cation exchanged zeolites (Amiridis *et al.*, 1993; Komatsu *et al.*, 1994) and have been added to TiO_2-pillared clays (Yang & Li, 1995).

2.3.2 Selective Non-Catalytic Reduction (SNCR)

NOx reduction by NH_3 or urea in the presence of excess oxygen without catalysts is called as selective non-catalytic reduction (SNCR). It was found that SNCR units can reduce NOx levels up to approximately 40% to 60%. When used in combination with other technologies, SNCR can produce low NOx concentrations (Busca *et al.*, 1998; Kapteijn *et al.*, 1996). SNCR exploits the reducing capability of ammonia to reduce NOx to nitrogen. If urea is the reduction agent, it decomposes to ammonia, which reacts with the NOx. SNCR tends to work over a narrow temperature range. The optimum is approximately 930°C to 1060°C (Rashidzadeh, 2004).

Normally for the SNCR processes was done by injecting amines (–NH–) or cyanides (–CN–) containing selective reducing agents such as ammonia, urea, or cyanuric acid (Rota and Zanoelo, 2003; Lee *et al.*, 2005).. These chemicals were found to be most effective at low, intermediate, and high oxygen concentrations, respectively (Caton & Zhiyong, 2004). The reaction of NO and ammonia only occurs after a minimum temperature, while ammonia decomposes to NO at higher temperatures. Thus the reaction needs a specific temperature window to be efficient. Further, the reaction also needs sufficient reaction time in that temperature window and need to be sufficiently mixed to avoid ammonia slip (Javed *et al.*, 2007). It has been reported that injection of some additives together with the reducing agents in SNCR processes can lower and widen the optimum reaction temperature window for