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MODELING AND SIMULATION OF A HYDROGEN-SELECTIVE CATALYTIC REDUCTION OF NITRIC OXIDE OVER A CARBON CATALYST

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Dedicated to my beloved parents, family and friends, who always bestow me sustainable motivations and encouragements

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ABSTRACT

Nitrogen oxides are a group of extremely reactive, toxic gases. Automobiles, trucks, and other non-road vehicles all emit NO_x pollution. An air pollutant is any gas or particulate at a concentration that is high enough to be harmful to life, environment and/or property. Significant progress has been made in the economy sector in terms of monitoring NO_x using both ground-based and space-borne sensors in the last decade. These data have enabled the detection of trends and seasonality, as well as the identification of emission sources and the study of the chemistry and dynamics that govern NO_x levels in the environment. Emissions are reduced using catalytic converters. There are various studies regarding selective catalytic reduction (SCR) in which, most of it is conducted experimentally. By reviewing all the recent literature studies, there are some limitations and complications, depending on the system, catalyst or the reductant. The overall aim of this research project is to simulate the selective catalytic reduction of nitric oxide using hydrogen as reductant and carbon as catalyst support. The effects of carbon catalyst and its catalytic activity on the conversion and selectivity of nitric oxide will be studied via this simulation. Specifically, this research project focuses on selective catalytic reduction of nitric oxide over a carbon catalyst using hydrogen as the reductant on square-opening honeycomb system. The model equations were derived according to the relativity to the project objectives which can be divided into several parts including energy balance, transport process and reaction rate. The model equations and parameters were then used to construct a 1-D computational fluid dynamics (CFD) simulation using Ansys software. Later, sensitivity analysis was performed on the catalytic material configurations using the constructed CFD model with engineering fundamentals. Hence, larger catalyst size contributed to a higher NO removal efficiency. From this thesis, 94.5% of NO content is reduced by carbon catalyst of 6mm x 6mm square length.

ABSTRAK

Nitrogen oksida ialah sekumpulan gas toksik yang sangat reaktif. Kereta, trak dan kenderaan berat yang lain, semuanya mengeluarkan pencemaran NO_x. Bahan pencemar udara ialah sebarang gas atau zarah pada kepekatan yang cukup tinggi untuk memudaratkan kehidupan manusia, alam sekitar dan/atau harta benda. Kemajuan ketara telah dicapai dalam sektor ekonomi dari segi pemantauan NO_x menggunakan kedua-dua penderia berasaskan *ground-based* dan *space-borne* dalam dekad yang lalu. Data ini telah membolehkan pengesanan arah aliran dan bermusim, serta pengenalpastian sumber pelepasan dan kajian kimia dan dinamik yang mengawal tahap NO_x dalam persekitaran. Pelepasan dikurangkan menggunakan penukar pemangkin. Terdapat pelbagai kajian mengenai pengurangan pemangkin terpilih di mana, kebanyakannya dijalankan secara eksperimen. Dengan mengkaji semua kajian terkini, terdapat beberapa batasan dan komplikasi, bergantung pada sistem, pemangkin atau reduktor. Matlamat keseluruhan projek penyelidikan ini adalah untuk mensimulasikan pengurangan pemangkin terpilih nitrik oksida menggunakan hidrogen sebagai reduktor dan karbon sebagai sokongan mangkin. Kesan pemangkin karbon dan aktiviti pemangkinnya terhadap penukaran dan selektiviti nitrik oksida akan dikaji melalui simulasi ini. Secara khusus, projek penyelidikan ini memberi tumpuan kepada pengurangan pemangkin terpilih oksida nitrik ke atas mangkin karbon menggunakan hidrogen sebagai reduktor pada sistem *square-opening honeycomb*. Persamaan model diperolehi mengikut relativiti kepada objektif projek yang boleh dibahagikan kepada beberapa bahagian termasuk keseimbangan tenaga, proses pengangkutan dan kadar tindak balas. Persamaan dan parameter model kemudiannya digunakan untuk membina simulasi dinamik bendalir pengiraan 1-D menggunakan perisian Ansys. Kemudian, analisis sensitiviti telah dilakukan pada konfigurasi bahan pemangkin menggunakan model CFD yang dibina dengan asas kejuruteraan. Oleh itu, saiz mangkin yang lebih besar menyumbang kepada kecekapan penyingkiran NO yang lebih tinggi. Daripada tesis ini, 94.5% kandungan NO dikurangkan oleh mangkin karbon dengan panjang persegi 6mm x 6mm.

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LIST OF SYMBOLS

cpsi	-	Number of cells per square inch
D	-	Outer diameter
δ	-	Wall thickness
g	-	Gravity acceleration
q	-	Energy
ρ	-	Density
P	-	Pressure
Γ	-	Reynolds number
t	-	Time
T	-	Temperature
U	-	Fluid velocity
x	-	Mass fraction

LIST OF ABBREVIATIONS

AC	-	Activated carbon
CAD	-	Computer-aided design
CFD	-	Computational fluid dynamics
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
DEF	-	Diesel exhaust fluid
DP	-	Differential pressure
EGR	-	Exhaust gas recirculation
EPA	-	Environmental Protection Agency
ERA	-	Explosion risk analysis
GAC	-	Granular activated carbon
HC	-	Hydrocarbon
H_2O	-	Water
HP	-	High pressure
LP	-	Low pressure
NAAQS	-	National ambient air quality standards
NHO_3	-	Nitric acid
N_2	-	Nitrogen
NH_3	-	Ammonia
NO	-	Nitric oxide
NO_x	-	Nitrogen oxides
O_2	-	Oxygen
ODE	-	Ordinary differential equation
ORR	-	Oxygen reduction reaction
PCM	-	Pulse code modulation
PDE	-	Partial differential equation
PEMB	-	Pre-engineered metal buildings
PM	-	Particulate matter
SCR	-	Selective catalytic reduction
SNCR	-	Selective non-catalytic reduction
SO_2	-	Sulphur dioxide

CHAPTER 1

INTRODUCTION

1.1 Background

Nitrogen oxides (NO_x) are a group of extremely reactive, toxic gases. It can be created naturally, for example, during the metabolism of certain soil microbes. When a fuel is burned at high temperatures, several gases are produced. For instance, during the combustion of flue gas, coexisting pollutants such as nitrogen oxides and mercury are basically found (Huang et al., 2021). Even automobiles, trucks, and other non-road vehicles all emit NO_x pollution. Focusing on air pollutant, it is any gas or particulate at a concentration that is high enough to be harmful to life, environment and/or property. A pollutant may originate due to natural or anthropogenic activities, sometimes both. Nitrogen oxides are created primarily from nitrogen (N_2) and oxygen (O_2) during high-temperature fuel combustion in automobiles (Brusseau et al., 2019). It is one of the six criterion air pollutants that have negative effects on people and ecosystems, thus affecting the surrounding air quality severely. Kumar (2022) stated that air quality has deteriorated as a result of increased ambient levels of air pollutants, particularly NO_x, over the last three decades as a result of fast industrial development. Besides, nitric oxide (NO) generates a reddish-brown haze in metropolitan air, which can cause heart and lung problems as well as be carcinogenic (Vakkilainen, 2021; Pronobis, 2020). Such circumstances occur because nitrogen oxides react with water to form nitric acid (HNO_3) and other acids, which is then contributed to acid rain.

Due to such environmental risks, the significant growth of legislative and regulatory actions happened and the foundation for national air pollution regulation was firmly built. Since the effects of emissions on health and the environment is being studied widely, new control technologies are produced to minimize the implications. Even the society demands for a safe living environment as they clearly aware of the current situation, thus the regulations are always evolving to keep it under control. The Clean Air Act mandates that the Environmental Protection Agency (EPA) establish national ambient air quality standards (NAAQS) for nitrogen oxides and five other pollutants that are considered hazardous to human health and the environment (EPA, 2021). The other pollutants are ozone, particulate matter, carbon monoxide, sulphur dioxide, and lead. The law also requires the EPA to evaluate and revise the standards on a regular basis to ensure that they continue to offer adequate health and environmental protection. Besides, UNEP (2021) reported that, in order to accomplish air quality standards as well as public health, legislation for air quality control should be developed by integrating liability, open clarity, enforceability and public involvement. They also willing to help countries to strengthen the air quality governance and serve as a resource for countries seeking to address air pollution effectively, indirectly contributing to the implementations of the Sustainable Developments Goals (SDGs).

According to Kumar (2022) and Brusseau et al. (2019), significant progress has been made in the economy sector in terms of monitoring NO_x using both ground-based and space-borne sensors in the last decade. These data have enabled the detection of trends and seasonality, as well as the identification of emission sources and the study of the chemistry and dynamics that govern NO_x levels in the environment. In order to reduce the continuous emissions of these air pollutants, catalytic converters are used. It is a compact, long-lasting, dependable, and the cost of the component is low (Thakur, 2019). The catalytic converter oxidizes all the harmful gases with the support of catalyst for efficient performance. This converter system usually has several approaches to achieve desired reactions. For instance, the primary approaches, based on furnace process adjustment, and secondary methods, based on flue gas treatment with appropriate reacting chemicals, are used to reduce NO_x concentration in flue gas. Almost all primary systems rely on the two basic processes of air staging and air-fuel staging, which are sometimes supplemented by recirculation of exhaust gases to the combustion area (Lopatin, 2020; Pronobis, 2020). Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are the two primary processes that secondary approaches are based on. Jiang et al. (2018) proposed that technology developments and changes in human activity patterns, in addition to emission restrictions, affect energy demand, industrial operations, commodities transportation, and automobile travel, all of which have significant and intricate influence on pollutant emissions.

1.2 Problem Statement

There are various studies regarding selective catalytic reduction (SCR) most of which are experimental. There are some limitations and complications, depending on the system, catalyst or the reductant. By all means, these challenges motivates to conduct simulation study on a particular reductant and catalyst support than the existing ones from the recent study research. For instance, most of the researchers use ammonia as the reductant which have been years now. However, its conversion efficiency always varies as the time passes. Thus, new selection of reductant need to be studied as an alternative so that more options will be available. Besides, lacking in modeling and simulation study pull out another struggle for not having enough guidance and validation of results. Despite facing technological advancements, experimental studies are still being preferred compared to simulation studies. Additionally, conducting hydrogen-selective catalytic reduction of nitric oxide at lab experimental scale is not at all easy, considering the fact that major elements and gaseous from the experiment is of high toxicity, very reactive as well as expensive (Vakkilainen, 2021; Pronobis, 2020). Considering about the high risk level, modeling and simulation studies are far much safer to be conducted.

Therefore, alternative to lab experimental method is required. It should be less-risk involved and has no harm to humans and environment as well as efficient enough to make justifications from the output result. Since common reductant such as ammonia have been widely used, it is better to seek out for new element so that more options will be available in the future. Even the catalyst selection plays an important role in increasing the efficiency of nitric oxide conversion. Besides, there are quite limited researches which focus on the selective catalytic reduction of nitric oxide using hydrogen as reductant and carbon as catalyst support. Among the limited researches, not many have opt for both, hydrogen reductant and carbon catalyst. Additionally, there are also insufficient study available to examine the multiple catalyst reactivity on selective catalytic reduction of nitric oxide by means involving lab experimental scale along with the usage of various engineering software applications. Even if it does, most of the results data are kept hidden due to plagiarism issues. However, the thesis will be conducted with guidance from the readily available journal sources and validated with supporting references. Therewith, this study will mainly focus on the modeling and simulation of a hydrogen-selective catalytic reduction of nitric oxide over a carbon catalyst using Ansys simulation software.

1.3 Research Questions

This project will focus on the study of modeling and simulation of a hydrogen-selective catalytic reduction of nitric oxide over a carbon catalyst and the research questions are studied.

i. How will the existing study contribute in modeling the reaction rates, energy balance, and species transport?
ii. How the simulation software used able to construct the expected design model by inputting all the necessary model equations such as heat and mass transfer, and reaction kinetics?
iii. How can the output results from the simulation software and model equations be associated with catalytic material configurations particularly carbon catalyst?

1.4 Objectives of the study

The overall aim of this research project is to simulate the selective catalytic reduction of nitric oxide using hydrogen as the reductant and carbon as the catalyst support. The effects of carbon catalyst and its catalytic activity on the conversion and selectivity of nitric oxide will be studied via simulation software. Specifically, this research project focuses on selective catalytic reduction of nitric oxide over a carbon catalyst using hydrogen as the reductant on square-opening honeycomb system. Thus, this will be achieved by the successful fulfilment of the following objectives:

i. To model the reaction rates, energy balance, and species transport based on the existing study.
ii. To construct a 1-D computational fluid dynamics (CFD) simulation using Ansys software.
iii. To perform sensitivity analysis on the catalytic material configurations using the constructed CFD model.

1.5 Scopes of the study

This research project emphasizes on hydrogen-selective catalytic reduction of nitric oxide over a carbon catalyst on square-opening honeycomb system. The model equations were derived according to the selected system which can be divided into several parts including energy balance, heat and mass transfer, transport process and reaction rate. The values were extracted separately from different sources hence the equations are consolidated. The model equations and parameters were then used to construct a 1-D computational fluid dynamics (CFD) simulation with the knowledge of the reactor design. Later, sensitivity analysis was performed on the catalytic material configurations using the constructed CFD model to observe the effects on the conversion and selectivity of nitric oxide.

1.6 Significance of study

In 2019, nitrous oxide emissions in Malaysia was 13,020 thousand metric tons of CO_2 equivalent (Knoema, 2022). Nitrous oxide emissions of Malaysia increased from 7,440 thousand metric tons of CO_2 equivalent in 1996 to 13,020 thousand metric tons of CO_2 equivalent in 2019. It shows an average annual rate of 2.43%. **Figure 1.1** is presented below the nitrous oxide emissions (thousand metric tons of CO_2 equivalent) in Malaysia from the year 1970 till 2018.

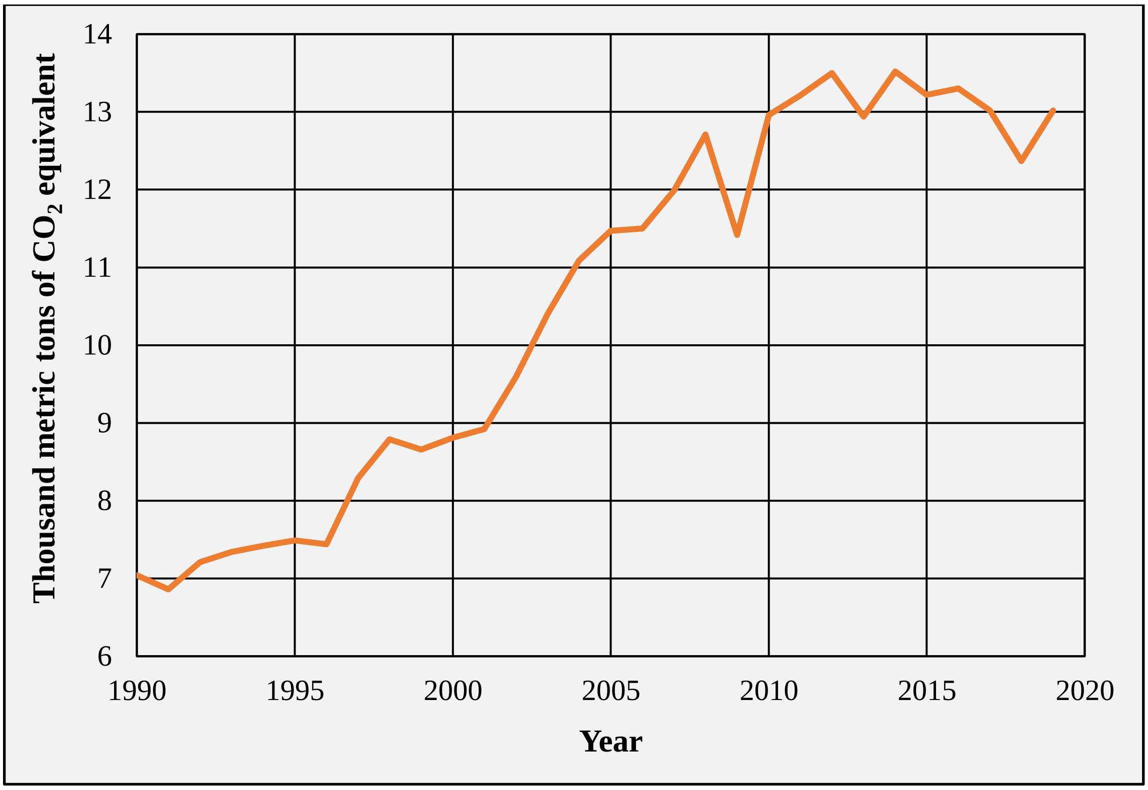

Figure 1.1: The nitrous oxide emissions (thousand metric tons of CO_2 equivalent) in Malaysia from the year 1990 till 2019 (World Bank Group, 2022).

As precursors in the creation of ozone and secondary aerosols, nitrogen oxides emissions have a significant impact on air quality and climate change. Based on Jiang et al. (2018), when comparing top-down estimates from satellites and surface NO_2 measurements to the trends anticipated by the US Environmental Protection Agency's emission inventory data, we find that NO_x emissions have not decreased as expected in recent years (1999-2018). There are several significance based on the findings resulted from this research project which are stated as follows:

i. The in-depth understanding on the catalytic behaviour of carbon catalyst that can help to increase the efficiency of nitric oxide conversion via hydrogen-selective catalytic reduction.
ii. The results acquired from the model equations and parameters based on the existing study are significant information for the construction of simulation design.

iii. The findings provide the reliable model equations such as energy balance, transport process and reaction rate to aid in better simulation to perform sensitivity analysis on the catalytic material configurations.

1.7 Summary

This chapter introduces nitric oxides as one of the major air pollutants that have negative effects on people and ecosystems. Air quality has deteriorated as a result of increased ambient levels of air pollutants, particularly NO_x, over the last three decades as a result of fast industrial development. Since the effects of emissions on health and the environment is being studied widely, new control technologies are produced to minimize the implications. Even the society demands for a safe living environment as they clearly aware of the current situation, thus the regulations are always evolving to keep it under control. Selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are the two primary processes that secondary approaches are based on in order to treat the flue gas with appropriate reacting chemicals and reduce NO_x concentration. Accordingly, modeling and simulation of selective catalytic reduction of nitric oxide is introduced in this research in order to study hydrogen-selective catalytic reduction of nitric oxide over a carbon catalyst on square-opening honeycomb system. Correspondingly, the findings acquired from this study will be utilised to correlate with the conversion and selectivity of nitric oxide.

CHAPTER 2

LITERATURE REVIEW

2.1 Selective catalytic reduction (SCR)

Selective catalytic reduction (SCR) is the most efficient technology to reduce the nitrogen oxides (NO_x) emissions from power stations, chemical industries, factories and automobiles which have contributed the most in contaminating the atmosphere. It is an advanced active emissions control technology system that injects a liquid-reductant agent into the exhaust stream of a diesel engine through a specific catalyst. As for the recent times, Han et al. (2019a) and Lai et al. (2018) stated that the reducing agent that has been commercially implemented in stationary source combustion units is SCR with ammonia (NH_3) as the units require a higher removal efficiency of NO_x. Automotive-grade urea, also known as diesel exhaust fluid (DEF), is commonly used as a reductant. Even Marberger et al. (2018) used SCR by NH_3 to reduce the emission of nitrogen oxide (NO) from diesel engines. It initiates a chemical reaction that transforms nitrogen oxides to nitrogen, water, and trace amounts of carbon dioxide (CO_2), which is then ejected through the vehicle tailpipe.

Ning et al. (2018) conducted a study the designation of the controller of the selective catalytic reduction system to meet the national fifth emission standard. The study is carried out both experimentally and simulation-based. Using MATLAB/Simulink, the SCR catalyst model and the open loop control system model are created, and the accuracy of the control model is verified through experiments. On the other hand, Lu and Huikang (2018) applied selective catalytic reduction system through CAN bus to study the relation between the velocity of ultrasonic wave, the concentration and temperature of urea solution, in which SCR provides an efficient guidance on vehicle exhaust treatment. In NH_3-SCR technology, catalysts are critical; $V_2O_5/WO_3/TiO_2$ catalysts have demonstrated high catalytic performance in stationary plants such as power plants and refineries Liu et al. (2019). Not to deny that, using NH_3 as a reductant (NH_3-SCR) for SCR of NO_x is considered one of the most efficient approaches.

2.1.1 Review of the system

Selective catalytic reduction (SCR) is a well-established emissions control system for stationary and mobile sources all over the world. According to Herrero and Ullah (2020), SCR of NO_x using ammonia is a well-established technology for reducing NO_x emissions from industrial and utility plants, as well as incinerators of industrial and municipal waste and nitric acid plants. The SCR system, which uses a reductant agent to convert NO_x to nitrogen, was designed to reduce NO_x constantly in an oxygen-rich atmosphere (Bion et al., 2018). Any SCR-NH_3 previously described can be used with Vanadia supported on titania-based catalysts. Cu-based oxides are another type of catalyst that performs well in nitric acid plants. For NO_x abatement in diesel exhausts, the NH_3-SCR method is now the encouraged technology. However, a little amount of NH_3 may escape unreacted, a phenomenon known as ammonia slip. In most cases, a high ammonia slip is viewed as a sign of a failing SCR system (Somoano, 2019).

Selective catalytic reduction technology was introduced to diesel engines in order to meet current and future legislative requirements for lower CO_2 and NO_x emissions. Okubo and Kuwahara (2020) stated that, instead of using ammonia directly, urea is typically employed in a system known as the urea-SCR system. This is because ammonia is a hazardous substance and it needs severe care as well as proper management. To meet the criteria of IMO Tier III, the SCR system may keep the emitted NO_x concentration low by rapidly altering the injection rate of the urea solution in response to changes in the engine load. According to Tillman (2018), SCR technology has been utilised commercially in power plants in Japan since 1980 and in Germany since 1986, with low-sulphur coal and, in certain cases, medium-sulphur coal being burned at first. Demonstration and full-scale SCR systems were deployed in US coal-fired power stations burning high-sulphur coals during the 1990s. **Table 2.1** shows the system along with the type of reductant and its performance that have been gathered from the recent study.

Table 2.1: List of reductants and system performance.

No.	System (Type of reductant)	Configuration	Performance (Temperature)	References
1.	SCR (Ammonia)	Cordierite honeycomb	Conversion: 65% (270 °C)	Marberger et al. (2018)
2.	SCR (Ammonia)	Spinel structure	Conversion: 80% (170 °C)	Meng et al. (2018)
3.	SCR (Ammonia)	Monolith honeycomb	Conversion: 84% (340 °C)	Zheng et al. (2019)
4.	SCR (Ammonia)	Cordierite/Pt ceramic honeycomb	Conversion: 58% (320 °C)	Phaily et al. (2014)
5.	SCR (Ammonia)	Cordierite honeycomb ceramic	Conversion: 95% (350 °C)	Nie et al. (2022)
6.	SCR (Ammonia)	Monolithic honeycomb	Conversion: 93% (150 °C)	Wang et al. (2018)
7.	SCR (Ammonia)	Monolithic honeycomb red mud	Conversion: 90% (350 °C)	Chen et al. (2021)
8.	SCR (Ammonia)	Red mud based-powdery/honeycomb	Conversion: 98% (400 °C)	Huangfu et al. (2019)
9.	SCR (Ammonia)	Spinel compound with honeycomb structure	Conversion: 85% (500 °C)	Ko et al. (2022)
10.	SCR (Ammonia)	Monolithic honeycomb	Conversion: 70% (400 °C)	Li et al. (2021)
11.	SCR (Carbon monoxide)	Monolithic mullite honeycomb	Conversion: 96.8% (250 °C)	Li et al. (2022)

2.1.2 Review of the catalyst

The catalyst is the most important component of SCR technology, since it dictates the system's denitrification efficiency and economic viability. Based on the research by Han et al. (2019a), major number of catalysts react negatively in the presence of strong sulphur dioxide (SO_2), thus reducing the NO conversion. This is because of reduction of SO_2 adsorption, weak alkalinity, poor interaction between SO_2 and catalyst, catalyst