



**REMOVAL OF NITRIC OXIDE (NO) BY SELECTIVE
CATALYTIC REDUCTION OVER MODIFIED OIL PALM
EMPTY FRUIT BUNCH FIBRES (EFB)**

by

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TABLE OF CONTENTS

| | PAGE |
|--|--------------|
| DECLARATION OF THESIS | i |
| TABLE OF CONTENTS | iii |
| LIST OF TABLES | viii |
| LIST OF FIGURES | xi |
| LIST OF ABBREVIATIONS | xiv |
| LIST OF SYMBOLS | xv |
| ABSTRAK | xvii |
| ABSTRACT | xviii |
| CHAPTER 1 : INTRODUCTION | 1 |
| 1.1 Research Background | 1 |
| 1.1.1 Nitric oxide (NO) pollution | 1 |
| 1.1.2 NO emission control technologies | 2 |
| 1.1.3 Oil palm waste as precursors of activated carbon | 4 |
| 1.2 Problem Statement | 5 |
| 1.3 Research Objectives | 7 |
| 1.4 Scope of Research | 8 |
| 1.5 Thesis Organization | 9 |
| CHAPTER 2 : LITERATURE REVIEW | 11 |
| 2.1 NO Emissions and Effects to Human and Environment | 11 |
| 2.2 NO Control Strategies | 13 |
| 2.2.1 Selective catalytic reduction | 14 |

| | | |
|--------------------------------|--|-----------|
| 2.2.2 | Selective non-catalytic reduction | 15 |
| 2.2.3 | Adsorption | 17 |
| 2.3 | Carbonaceous Materials for NO Removal | 20 |
| 2.3.1 | Properties of carbonaceous material | 20 |
| 2.3.2 | Oil palm agricultural waste as the source of carbonaceous material | 22 |
| 2.3.3 | Activation of carbonaceous material | 24 |
| 2.3.3.1 | Physical activation | 24 |
| 2.3.3.2 | Chemical activation | 26 |
| 2.4 | Performance of Activated Carbon Modified with Metal Additives | 29 |
| 2.4.1 | Initial gas concentration | 34 |
| 2.4.2 | Presence of other gases | 34 |
| 2.4.3 | Moisture | 35 |
| 2.4.4 | Reaction temperature | 36 |
| 2.4.5 | Metal loading | 37 |
| 2.5 | Mechanism of NO Removal over Metal-Modified AC | 37 |
| 2.6 | Adsorption Equilibrium | 39 |
| 2.6.1 | Fixed bed adsorption | 40 |
| 2.6.2 | Gas adsorption | 42 |
| 2.7 | Adsorption Isotherm | 43 |
| 2.8 | Adsorption Kinetics | 46 |
| 2.9 | Adsorption Thermodynamics | 48 |
| 2.10 | Adsorption Diffusional Mechanism | 49 |
| 2.10.1 | Intraparticle diffusion model | 50 |
| CHAPTER 3 : METHODOLOGY | | 52 |
| 3.1 | Research Flow | 52 |

| | | |
|---|---|-----------|
| 3.2 | Materials and Chemicals | 54 |
| 3.3 | Sample Preparations | 54 |
| 3.3.1 | Phosphoric acid activation of raw EFB | 55 |
| 3.3.2 | Metal impregnation onto EFBC | 56 |
| 3.4 | NO Breakthrough Study | 57 |
| 3.4.1 | Experimental set-up | 57 |
| 3.4.2 | Experimental procedure | 59 |
| 3.4.3 | Variations of the operating conditions | 61 |
| 3.4.4 | Adsorption isotherm | 63 |
| 3.4.5 | Adsorption kinetics | 64 |
| 3.4.6 | Adsorption thermodynamics | 65 |
| 3.4.7 | Hydrogen pre-treatment | 66 |
| 3.5 | Characterization techniques | 66 |
| 3.5.1 | Proximate analysis (TGA-DTG analysis) | 67 |
| 3.5.2 | Ultimate analysis | 67 |
| 3.5.3 | Surface morphology | 68 |
| 3.5.4 | Surface area and pore characterization | 68 |
| 3.5.5 | Phase identification and crystallite structure/size | 69 |
| 3.5.6 | Surface functional groups | 69 |
| 3.5.7 | Temperature programme reduction (TPR) | 70 |
| 3.5.8 | Temperature programme desorption (TPD) | 71 |
| CHAPTER 4 : RESULTS AND DISCUSSION | | 72 |
| 4.1 | Activation of Oil Palm Empty Fruit Bunch (EFB) | 72 |
| 4.1.1 | Influence of carbonization temperature on surface area and pore characteristics | 73 |

| | | |
|---------|---|-----|
| 4.1.2 | Changes in surface morphology with different carbonization temperatures | 77 |
| 4.1.3 | NO removal at different carbonization temperatures | 78 |
| 4.2 | Impregnation of Metal Catalysts onto EFBC | 82 |
| 4.2.1 | Type of metal catalysts | 82 |
| 4.2.2 | Variations in metal loading | 84 |
| 4.3 | Characterisation of Raw EFB, EFBC and CuO/EFBC | 87 |
| 4.3.1 | Proximate and ultimate analysis | 87 |
| 4.3.2 | Surface area and pore characteristics | 92 |
| 4.3.3 | Surface morphology | 95 |
| 4.3.4 | Surface chemistry | 96 |
| 4.4 | NO Adsorption Behaviour, Kinetics and Mechanism | 100 |
| 4.4.1 | Influence of NO initial concentration on NO removal | 100 |
| 4.4.2 | Role of reaction temperature on NO removal | 104 |
| 4.4.3 | Adsorption isotherm | 110 |
| 4.4.4 | Adsorption kinetics | 114 |
| 4.4.5 | Adsorption thermodynamics | 123 |
| 4.5 | Hydrogen (H ₂) Pre-treatment at Different Temperatures on CuO/EFB | 126 |
| 4.5.1 | Characterization of hydrogen pre-treated EFBC and CuO/EFBC | 126 |
| 4.5.1.1 | Surface area and pore characteristics | 126 |
| 4.5.1.2 | Surface morphology | 131 |
| 4.5.1.3 | Surface functional groups | 133 |
| 4.5.1.4 | Crystallite structure and size | 135 |
| 4.5.1.5 | Temperature program reduction (TPR) | 138 |
| 4.5.1.6 | Temperature program desorption (TPD) | 140 |

| | | |
|---------------------------------------|--|------------|
| 4.5.2 | NO breakthrough study on CuO/EFBC and H ₂ -pretreated samples | 143 |
| CHAPTER 5 : CONCLUSION | | 150 |
| 5.1 | Conclusion | 150 |
| 5.2 | Recommendations | 153 |
| REFERENCES | | 154 |
| APPENDIX A LIST OF PUBLICATION | | 176 |

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LIST OF TABLES

| | PAGE | |
|-----------|--|----|
| Table 2.1 | Primary energy supply of Malaysia for 2017 and 2018 | 12 |
| Table 2.2 | Application of oil palm EFB activated carbon | 24 |
| Table 2.3 | Physical activation of various low-cost raw materials for NO/NO ₂ removal | 26 |
| Table 2.4 | Chemical activation of various raw materials for NO/NO ₂ removal | 27 |
| Table 2.5 | Parameters and performance of various activated carbon for NO removal | 30 |
| Table 2.6 | Adsorption isotherm models for NO removal | 44 |
| Table 2.7 | Adsorption kinetic models for NO removal | 47 |
| Table 3.1 | Operating parameters during NO breakthrough experiments | 61 |
| Table 3.2 | Adsorption isotherm model equations | 63 |
| Table 3.3 | Adsorption kinetic model equations | 64 |
| Table 3.4 | Thermodynamics models equations | 65 |
| Table 4.1 | BET characteristics of EFBC carbonized at different temperature | 74 |
| Table 4.2 | NO adsorption capacities of EFBC at different carbonisation temperatures | 79 |
| Table 4.3 | Breakthrough time, saturation time and NO adsorption capacity of EFBC impregnated with different metal catalysts | 83 |

| | | |
|------------|---|-----|
| Table 4.4 | NO adsorption capacity over EFBC modified with different metal loading | 85 |
| Table 4.5 | Proximate and ultimate analysis for EFB, EFBC and CuO/EFBC | 90 |
| Table 4.6 | Surface area and pore characteristics of EFBC and CuO/EFBC | 94 |
| Table 4.7 | Summary of band assignments for EFB, EFBC, CuO/EFBC and CuO/EFBC + NO | 98 |
| Table 4.8 | Breakthrough time, saturation time and NO adsorption capacity of EFBC and CuO/EFBC at different initial NO concentrations | 102 |
| Table 4.9 | Comparison of EFBC and CuO/EFBC with various other adsorbents in terms of influence of initial NO concentration | 104 |
| Table 4.10 | Breakthrough time, saturation time and NO adsorption capacity of EFBC and CuO/EFBC at different reaction temperatures | 106 |
| Table 4.11 | Comparison of EFBC and CuO/EFBC with various adsorbents in terms of the influence of reaction temperature | 108 |
| Table 4.12 | Nitrogen concentration in the effluents of NO breakthrough experiment conducted at 100 and 300°C | 109 |
| Table 4.13 | Parameters and constants of the isotherm models fitted for EFBC and CuO/EFBC for different initial | 112 |
| Table 4.14 | Kinetic parameters and coefficients for NO removal by EFBC and CuO/EFBC | 117 |
| Table 4.15 | Parameters/coefficients from linear fitting of NO removal by EFBC and CuO/EFBC with intra-particle diffusion model | 121 |
| Table 4.16 | Arrhenius and other thermodynamic parameters | 124 |

| | | |
|------------|---|-----|
| Table 4.17 | Surface area and pore characteristics of fresh EFBC, CuO/EFBC | 129 |
| Table 4.18 | EDX elemental analysis of fresh CuO/EFBC and H ₂ pre-treated samples | 132 |
| Table 4.19 | Crystallite size and structure for fresh CuO/EFBC and H ₂ pre-treated samples | 138 |
| Table 4.20 | H ₂ consumption of CuO/EFBC and H ₂ pre-treated samples | 139 |
| Table 4.21 | The properties of reducibility, basicity and acidity surface chemistry of untreated CuO/EFBC and H ₂ treated samples | 141 |
| Table 4.22 | Breakthrough time (at C/C ₀ = 0.05) and saturation time and adsorption capacity at C/C ₀ = 0.5 and 0.95 | 144 |

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LIST OF FIGURES

| | PAGE | |
|------------|--|----|
| Figure 2.1 | Total energy consumption in Malaysia from 2009 to 2018 | 12 |
| Figure 2.2 | (a) Sketch of oil palm FFB; (b) Cross section of FFB with its fibre arrangement (Adapted from Shinoj, Visvanathan, Panigrahi, & Kochubabu (2011)) | 23 |
| Figure 2.3 | Breakthrough curve for a gas single component. | 41 |
| Figure 3.1 | Flowchart of the overall process in the study of NO removal by modified oil palm empty fruit bunch | 53 |
| Figure 3.2 | Schematic diagram of experimental set-up for NO breakthrough | 57 |
| Figure 3.3 | Experimental set-up | 58 |
| Figure 3.4 | Packed bed quartz-column (15 mm ID and 250 mm length) | 59 |
| Figure 4.1 | Nitrogen adsorption/ desorption isotherm of EFBC at different temperature of carbonization | 73 |
| Figure 4.2 | Mesopore (a) and micropore (b) size distributions of EFBC at various carbonisation temperatures obtained using BJH and MP methods | 76 |
| Figure 4.3 | SEM micrographs of precursor and activated EFB at different carbonisation temperature from 400-550°C at 5000x magnification: (a) raw EFB (b) EFBC-400 (c) EFBC-450 (d) EFBC-500 and (e) EFBC-550 | 78 |
| Figure 4.4 | NO breakthrough at different carbonization temperatures of EFBC | 79 |

| | | |
|-------------|--|-----|
| Figure 4.5 | NO breakthrough of EFBC impregnated with different metal catalysts | 82 |
| Figure 4.6 | NO breakthrough curve at different metal loading | 85 |
| Figure 4.7 | TGA/DTG curve for (a) raw EFB, (b) EFBC and (c) CuO/EFBC | 89 |
| Figure 4.8 | Nitrogen adsorption/ desorption isotherm for EFBC and CuO/EFBC | 93 |
| Figure 4.9 | Pore diameter distribution (PSD) of EFBC and CuO/EFBC | 95 |
| Figure 4.10 | SEM micrographs showing the morphology of (a) EFBC and (b) CuO/EFBC | 96 |
| Figure 4.11 | EDX spectrum of CuO/EFBC | 96 |
| Figure 4.12 | FTIR spectrometry of EFB, EFBC, CuO/EFBC and CuO/EFBC + NO | 97 |
| Figure 4.13 | NO breakthrough curve for (a) EFBC and (b) CuO/EFBC samples at different initial NO concentrations | 101 |
| Figure 4.14 | NO breakthrough curve of (a) EFBC and (b) CuO/EFBC at different reaction temperatures | 105 |
| Figure 4.15 | Nonlinear plots of Langmuir, Freundlich, Temkin, Redlich-Peterson, Toth and Sips isotherm models for NO adsorption on (a) EFBC and (b) CuO/EFBC | 111 |
| Figure 4.16 | Non-linear plots of kinetic models (pseudo-first order, pseudo-second order and Avrami) for NO removal by EFBC as a function of temperatures: (a) EFBC (100°C), (b) EFBC (150°C), (c) EFBC (200°C) (d) EFBC (250°C) and (e) EFBC (300°C) | 115 |
| Figure 4.17 | Non-linear plots of kinetic models (pseudo-first order, pseudo-second order and Avrami) for NO removal by | |

| | | |
|-------------|---|-----|
| | CuO/EFBC as a function of temperature: (a) CuO/EFBC (100°C), (b) CuO/EFBC (150°C), (c) CuO/EFBC (200°C) (d) CuO/EFBC (250°C) and (e) CuO/EFBC (300°C) | 116 |
| Figure 4.18 | Plots of intra-particle diffusion model for NO removal by EFBC and CuO/EFBC from 100 to 300°C: (a) overall intra-particle diffusion plot (b) zoom in of plot of region I and region II (Initial NO concentration: 500 ppm; Total flow rate: 100 mL/min) | 120 |
| Figure 4.19 | Arrhenius plots for NO removal by (a) EFBC and (b) CuO/EFBC | 123 |
| Figure 4.20 | Nitrogen adsorption/desorption of (a) EFBC and CuO/EFBC; (b) CuO/EFBC and H ₂ pre-treated samples | 127 |
| Figure 4.21 | Pore diameter distribution (PSD) of CuO/EFBC and all hydrogen pre-treated samples | 130 |
| Figure 4.22 | Surface morphologies of fresh CuO/EFBC and H ₂ pre-treated samples | 131 |
| Figure 4.23 | FTIR spectra for CuO/EFBC and H ₂ pre-treated samples | 133 |
| Figure 4.24 | XRD profile for CuO/EFBC and H ₂ pre-treated samples | 136 |
| Figure 4.25 | H ₂ -TPR profile of CuO/EFBC and H ₂ pre-treated samples | 139 |
| Figure 4.26 | (a) CO ₂ -TPD profile and (b) NH ₃ -TPD profile for CuO/EFBC and H ₂ pre-treated samples | 141 |
| Figure 4.27 | NO breakthrough curves of CuO/EFBC and H ₂ pre-treated samples | 144 |
| Figure 4.28 | Schematic representation of surface groups available at different H ₂ pre-treatment temperatures | 146 |

LIST OF ABBREVIATIONS

| | |
|-------|---|
| AC | Activated carbon |
| BET | Brunauer-Emmett-Teller |
| EDS | Energy-dispersive X-ray spectroscopy |
| EFB | Oil palm empty fruit bunch |
| EFBC | Oil palm empty fruit bunch carbon |
| FFB | Fresh fruit bunches |
| FTIR | Fourier Transform Infrared |
| IUPAC | International Union of Pure and Applied Chemistry |
| MFC | Mass flow controller |
| SEM | Scanning electron microscopy |
| SCR | Selective catalytic reduction |
| SNCR | Selective non-catalytic reduction |
| STA | Simultaneous thermal analyzer |
| VOC | Volatile Organic Compound |

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LIST OF SYMBOLS

| | |
|--------------------------|--|
| A | Arrhenius factor |
| A_T | Constant for Temkin isotherm |
| b_T | Constant for Temkin isotherm |
| B_t | Constant for Boyd model |
| C | Outlet concentration of adsorbate |
| C_e | Concentration of adsorbate at equilibrium |
| C_i | Constant for intraparticle diffusion model |
| C_0 | Initial concentration of adsorbate |
| C_t | Concentration of adsorbate at time, t |
| CuO | Copper oxide |
| D_p | Average pore diameter |
| E_a | Arrhenius activation energy of adsorption |
| F | Fraction of adsorbent adsorbed for Boyd model |
| $Fe(NO_3)_3 \cdot 9H_2O$ | Iron (III) nitrate nonahydrate |
| H_2SO_4 | Sulfuric acid |
| H_3PO_4 | Phosphoric acid |
| He | Helium |
| HNO_3 | Nitric oxide |
| k_1 | Adsorption rate constant for pseudo-first order |
| k_2 | Adsorption rate constant for pseudo-second order |
| k_{Av} | Avrami kinetic constant |
| K_F | Adsorption or distribution coefficient for Freundlich isotherm |
| K_L | Rate of adsorption for Langmuir isotherm |
| k_{pi} | Adsorption rate constant for intraparticle diffusion model |
| k_s | Sips isotherm model constant |
| Mtoe | Million tons of oil equivalent |
| N_2 | Nitrogen |
| NaOH | Sodium hydroxide |
| NH_3 | Ammonia |
| $NiSO_4 \cdot 6H_2O$ | Nickel (II) sulfate hexahydrate |

| | |
|------------------|---|
| NO | Nitric oxide |
| NO ₂ | Nitrogen dioxide |
| O ₂ | Oxygen |
| O–Cu | Oxygen species adsorbed on the catalytic active sites |
| P/P ₀ | Relative pressure |
| q | Adsorption capacity of adsorbent (mg/g) |
| R ² | Correlation coefficient value |
| t _B | Breakthrough point |
| wt.% | Percentage by weight |
| y _f | Mole fraction of NO |

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Penyingkiran Nitrik Oksida (NO) melalui Penurunan Bermangkin Memilih dengan Serat Tandan Kosong Buah Kelapa Sawit Terubahsuai (EFB)

ABSTRAK

Nitrik oksida (NO) merupakan salah satu pencemar utama yang disebarkan daripada pembakaran yang boleh menyumbang kepada banyak masalah persekitaran global lain seperti hujan asid dan kabut fotokimia. Disebabkan risiko yang berkaitan, usaha berterusan untuk mengkaji penyingkiran NO daripada punca industri adalah perlu terutamanya pada suhu rendah. Kajian ini bertujuan untuk menyiasat penyingkiran NO melalui penurunan bermangkin memilih menggunakan karbon teraktif yang berasal daripada tandan kelapa sawit (EFB) sebagai bahan sokong. Karbon teraktif (EFBC) tersebut disediakan melalui pengaktifan kimia satu peringkat menggunakan asid fosforik (H_3PO_4) dan dikarbonkan pada suhu antara $400-550^{\circ}C$ selama 4 jam. Suhu pengkarbonan yang lebih tinggi membawa kepada pembesaran liang dan menghasilkan kapasiti penjerapan NO yang lebih rendah. EFBC tersebut kemudiannya diresapi dengan bahan tambah iaitu oksida/garam kuprum (Cu), nikel (Ni) dan besi (Fe) melalui peresapan basah, dan pengkalsinan pada suhu $400^{\circ}C$. Penambahan sebanyak 5 wt.% CuO didapati memberi kesan yang lebih baik sedikit kepada penyingkiran NO berbanding dengan dua logam berbeza, dan CuO pada muatan yang lebih tinggi (10-20 wt. %). Sifat fizikal dan kimia bagi EFBC dan sampel yang diubahsuai telah dicirikan dengan analisis luas permukaan dan liang, analisis hampiran, morfologi permukaan dan kimia permukaan. Peningkatan kepekatan NO awal dan suhu tindak balas yang masing-masing dikaji antara 300-1000 ppm dan $100-300^{\circ}C$, didapati meningkatkan penyingkiran NO oleh EFBC dan CuO/EFBC. EFBC juga didapati menunjukkan prestasi yang baik dalam penguraian NO, dengan penghasilan N_2 yang lebih tinggi, manakala suhu tindak balas yang lebih tinggi meningkatkan pengeluaran CuO/EFBC dari 13.99 % ($100^{\circ}C$) kepada 62.56 % ($300^{\circ}C$). Penjerapan NO oleh EFBC dan CuO/EFBC pada $100^{\circ}C$ adalah sesuai dipadankan kepada isoterma Sips, yang menunjukkan sifat heterogen permukaan penjerap. Selain itu, data kinetik penjerapan NO oleh kedua-dua EFBC dan CuO/EFBC paling sesuai dipadankan dengan model kinetik Avrami, yang mencadangkan bahawa penjerapan NO dikawal terutamanya oleh proses lekatan permukaan dan resapan. Data penjerapan NO juga berpadanan dengan model resapan intrazarah melalui resapan intrazarah dan resapan sapat. Tindak balas ini bersifat endotermik dan tidak spontan, melibatkan kedua-dua laluan penjerapan fizikal dan kimia. Laluan yang terdahulu tersebut adalah dibantu oleh ciri-ciri fizikal seperti jumlah luas permukaan yang tinggi dan saiz liang yang lebih kecil manakala yang kemudiannya dipengaruhi oleh kimia permukaan pada permukaan karbon. Pra-rawatan hidrogen susulan bagi CuO/EFBC pada suhu $600-700^{\circ}C$ menghasilkan ciri-ciri luas permukaan spesifik dan isipadu liang yang lebih baik, mewujudkan lebih banyak kumpulan permukaan berbes dan kehadiran saiz kristal CuO, Cu_2O dan Cu_3P yang lebih kecil, yang menyumbang kepada penyebaran logam yang lebih tinggi, sesuai untuk penyingkiran NO. Hasil penyelidikan ini akan menyumbang ilmu pengetahuan dalam penyingkiran NO dan berguna dalam aplikasi pasca pembakaran, terutamanya bagi industri kecil sederhana yang tidak mampu membiayai teknologi penyingkiran NO bersuhu tinggi.

Removal of Nitric Oxide (NO) by Selective Catalytic Reduction over Modified Oil Palm Empty Fruit Bunch Fibres (EFB)

ABSTRACT

Nitric oxide (NO) is one of the primary air pollutants emitted from combustion which could lead to many other global environmental problems such as acid rain and photochemical smog. Due to the associated risks, continuing effort to study the NO removal from industrial sources are necessary especially at low temperature. This work aims to investigate the NO removal by selective catalytic reduction (SCR) using activated carbon originated from oil palm empty fruit bunch fibres (EFB) as support material. The activated carbon (EFBC) was prepared by one stage chemical activation using phosphoric acid (H_3PO_4) and carbonized at temperature between 400-550°C for 4 hours. Higher carbonization temperature led to pore enlargement and resulted in lower NO adsorption capacity. The EFBC was then impregnated with metal additives i.e. copper (Cu), nickel (Ni) and iron (Fe) oxides/salts via wet incipient impregnation, and calcined at 400°C. Introduction of 5 wt.% CuO was found to be slightly more favourable for NO removal in comparison to the other two metals, and CuO at higher loading (10-20 wt.%). The physical and chemical properties of EFB and modified samples were characterized with surface area and pore analysis, proximate analysis, surface morphology and surface chemistry. The increase in the initial NO concentration and reaction temperature investigated between 300-1000 ppm and 100-300 °C, respectively, were found to improve NO removal by both EFBC and CuO/EFBC. EFBC was also found to exhibit better performance in dissociative NO removal, with higher N_2 production, while higher reaction temperature increased N_2 production of EFBC from 13.99 % (100°C) to 62.56 % (300°C). The NO adsorption of both EFBC and CuO/EFBC at 100°C was best fitted to Sips isotherm, indicating the heterogenous nature of the adsorbent surface. On the other hand, the adsorption kinetic data of NO for both EFBC and CuO/EFBC were best fitted to Avrami kinetic model, suggesting that the NO adsorption were mainly governed by surface attachment and diffusional process. The NO adsorption data also fitted well with the intra-particle diffusion model via intraparticle diffusion and film diffusion. The reaction was endothermic in nature and nonspontaneous, involving both physisorption and chemisorption routes. The former route was mainly assisted by the physical characteristics such as higher surface area and smaller pore size while the latter were influenced by the surface chemistry on the carbon surface. Further hydrogen pre-treatment of CuO/EFBC at 600-700°C resulted in better specific surface area and pore properties, introduced more basic surface groups and induced the presence of smaller crystallite CuO, Cu_2O and Cu_3P , leading to higher metal dispersion favourable for NO removal. The research outcome will contribute to knowledge in NO removal and useful for post-combustion applications, especially for small medium industries who cannot afford high-temperature NO removal technologies.

CHAPTER 1 : INTRODUCTION

This chapter provides an overview of the research background including on air pollution especially nitric oxide (NO) emission, the effects to the human and the environment, the occurrence of NO and the needs for NO abatement. At the end of the chapter, the problem statement, research objectives and the scope of research, as well as the organization of the thesis are presented.

1.1 Research Background

1.1.1 Nitric oxide (NO) pollution

Nitric oxide (NO) is one of the oxides of nitrogen usually found together with a small fraction nitrogen dioxide (NO_2) which are collectively referred as nitrogen oxides (NO_x). NO and NO_2 can also be called 'fresh' nitrogen oxides since in these forms they reach atmosphere from a photochemical point. For the same reason, another prominent 'fresh' nitrogen oxide is N_2O . During the day, NO_2 is separated by UV light into NO molecule and O atom, which could then combine with molecular oxygen (O_2) to produce ground level ozone (O_3). In addition, ozone in the atmosphere could also oxidise NO to produce NO_2 . Finally, NO_2 may be oxidised into nitric acid (HNO_3 , vapour) which could be adsorbed on the ground before being converted into nitrates, or dissolves in cloud droplets. NO_2 is also converted into nitrates by different oxidation processes at night.

NO is primarily produced by the reaction between nitrogen and oxygen at elevated temperature either through manmade or natural processes. The anthropogenic

NO (from manmade process) is mostly generated by the combustion of fossil fuels in both mobile and stationary sources. A stationary source like incineration process contributes to the emission of about 95% of NO and 5% NO₂. The natural sources of NO include oxidation of NH₃, volcano eruption and lightning strike (Skalska et al. 2010).

NO is an 'air pollutant' which may be harmful not only to human, but also to animals, vegetation and building materials. The prevalence of primary pollutants in the atmosphere especially NO enhanced the environmental problems related to secondary pollutants such as the occurrence of acid rain, photochemical smog, greenhouse effect and even global warming which is caused by N₂O. Photochemical smog and acid rain may affect the human respiratory tracts including airway inflammation in human health (e.g. causing bronchitis and pneumonia) and the environment through acidification of soil and waters respectively.

Due to the adverse effects associated with NO, its emission limit expressed in NO₂, which is fully implemented in 2020 based on the current Malaysia Ambient Air Quality Standard (2013) is also very stringent, i.e. 0.28 ppm (280 µg/cm³) in an hour or 0.07 ppm (70 µg/cm³) in 24 hour. Therefore, an improvement in the method of NO removal from exhaust or flue gases is essential for industries emitting NO to meet the regulations meant for maintaining the human health and conserving the nature.

1.1.2 NO Emission Control Technologies

A number of technologies have been established to control NO emissions (Abdulrasheed et al., 2018; Cheng & Bi, 2014). The major technologies used are

combustion and catalytic technology. The combustion technology is achieved by optimizing the combustion process which is the main source of NO generation. The cost of this technology is still low, but the removal efficiency is also quite low (generally 30-40%) (Belhachemi, Jeguirim, Limousy, & Addoun, 2014; Srivastava, Hall, Khan, Culligan, & Lani, 2005). Therefore, there is a need for more efficient combustion technology or other end-of pipe technology which complements the combustion modifications. In a non-catalytic process or selective non-catalytic reduction (SNCR), a well-known NO reduction process operating in addition of ammonia (NH₃, or urea) injection to the flue gases can reduce NO to produce nitrogen and water up to 90% efficiency, however, a very narrow, high temperature range (850 - 950°C) is required.

On the other hand, the catalytic NO reduction technologies show a rather promising efficiency for reduction of NO emissions from stationary sources into the atmosphere. Selective catalytic reduction (SCR) uses a catalyst e.g. vanadium in the presence of an external reducing agent such as ammonia or urea at a lower temperature (250 - 400°C). With SCR using ammonia as reducing agent (NH₃-SCR), the NO reduction could reach up to about 94% efficiency (Cheng & Bi, 2014). Nevertheless, the conventional SCR methods remains as an expensive technology and this technique has disadvantages such as vanadia emissions, ammonia slipping and air heater fouling (Ghouma et al., 2018; Al-Rahbi, Nahil, Wu, & Williams, 2016 & Belhachemi et al., 2014)

In order to overcome this problem, a new material or method as alternative to ammonia-based reduction technology is preferable. The use of carbonaceous material like activated carbon which could be cheaply produced due to the abundance of raw material

has also become a popular choice in the research for SCR of NO (Zeng, Lu, Li, Mai & Zhang, 2012).

As activated carbon is known to have unique properties such as high surface area and bulk porosity, and various surface chemical properties, it has been recognised as a good support and reducing agent (Jeguirim, Belhachemi, Limousy & Bennici, 2018). Other than that, activated carbon can be modified by adding catalyst, in which the carbon could play the role as both catalyst support and reducing agent.

1.1.3 Oil palm waste as precursors of activated carbon

Being one of the world's top palm oil producers, a large amount of biomass is produced from oil palm plantation and milling activity by the oil palm industry in Malaysia. These include empty fruit bunches (EFB), fibre, shell, wet shell, palm kernel, fronds and trunks. In numbers, one hectare of oil palm plantation can produce about 50 to 70 tonnes of biomass residues (Onoja, Chandren, Abdul Razak, Mahat, & Wahab, 2018). The abundance of biomass from oil palm industry makes it has a very good potential to be commercialised into products such as animal food, fertilizer and also as adsorbent for environmental applications.

Many research works have been devoted in developing low cost adsorbents derived from oil palm industrial and agriculture waste (Onoja et al., 2018; Shu, Zhang, Wang, & Wang, 2018; Viena, Elvitriana, & Wardani, 2018). Production of adsorbent material from oil palm waste helps to reduce the accumulation of waste in the oil palm

plantations and industry. Furthermore, it is a waste to wealth approach as we reuse the waste materials for creating useful products.

1.2 Problem Statement

NO emitted from both stationary industrial sources and mobile vehicles are harmful to human health and environment. The well-known process of selective catalytic reduction (SCR) of NO with reducing agents such as urea and ammonia and catalyzed by vanadium on titanium dioxide (TiO_2) at 300 - 400°C is regarded as an effective de-NO technology. However, many problems exist in the application of SCR of NO by urea such as vanadia emission, ammonia slipping, air heater fouling, requirement for reheating of flue gas and high running cost (Ghouma et al., 2018; Al-Rahbi, Nahil, Wu, & Williams, 2016 & Belhachemi et al., 2014)

The use of carbon as the catalyst support in SCR technology has led to the study on carbonaceous material such as activated carbon and carbon nanotubes for removal of NO at low temperature (below 300°C) (Athappan, Sattler, and Sethupathi, 2015; Zeng et al., 2012; Wang, Huang, Shimohara, Kang and Liang, 2011). Since carbonaceous material used as catalyst support can also act as inexpensive and safer reducing agent, the carbon-based catalytic system can avoid the need for an external gaseous reducing agent. It could be a promising technique for the SCR of NO, where the emissions become colder, provided the catalyst life is extended, the catalytic properties are enhanced, and the cost of catalyst preparation is reduced.

The properties of the carbonaceous materials depend on several factors, mainly its preparation procedure (raw material, activating agent, etc) to produce porous texture, and surface chemistry. These factors strongly influence the transport phenomena in the carbon, adsorption and chemisorption characteristics, and the activation of molecules in catalytic reactions. It has been shown by previous work that phosphoric acid activation could produce carbons with high microporosity and incorporate surface groups which could be useful active sites in adsorption process. In addition, metal additives/catalysts deposition on the activated carbon could provide additional sites which are useful for dissociative NO adsorption. Most of the efficient metal catalysts used in SCR are noble metals e.g. Palladium (Pd), Platinum (Pt), Ruthenium (Ru), Khosravi et al., (2014) ; Wang et al., (2014) ; Tanaka, Okuhara, & Misono, (1994) ; Bosch & Janssen, (1988) which have high catalytic activity but are also high in cost. This leads to extensive work being done with non-precious metals catalysts e.g. Nickel (Ni), Cobalt (Co), Manganese (Mn), Copper (Cu), Lanthanum (La) and Cerium (Ce), Abdedayem, Guiza, & Ouederni, (2015a); Xiuyun Wang, Wen, Mi, Li, & Wang, (2015); Lu, Rau, Chen, Huang, & Wey, (2013); Chuang, Liu, & Wey, 2010; Kante, Deliyanni, & Bandosz, (2009) ; Grzybek, Klinik, Dutka, Papp, & Suprun, (2005) to improve the catalytic efficiency especially for low temperature applications. Among these, copper oxide catalysts are attractive as they exhibited high catalytic removal of NO at low temperature Bai, Li, Wang, Guan, & Jiang, (2013) especially when using activated carbon as support. However, the nature of the catalyst catalytic activity has not been fully discovered because of the complexity of surface chemistry and pore characteristics of activated carbon.

These motivations lead to this research being proposed to enhance the properties of the abundantly available local agricultural waste (i.e. oil palm empty fruit bunch)