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

by

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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

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_o	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
$Fe(NO_3)_3.9H_2O$	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
$NiSO_4.6H_2O$	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

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°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°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°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°C) kepada 62.56 % (300°C). Penjerapan NO oleh EFBC dan CuO/EFBC pada 100°C adalah sesuai dipadangkan 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 saput. 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°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 ºC, 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 % (100ºC) to 62.56 % (300ºC). 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 600-700ºC 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% NO_2. The natural sources of NO include oxidation of NH_3, 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 N_2O. 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 NO_2, 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 $\mu g/cm^3$) in an hour or 0.07 ppm (70 $\mu g/cm^3$) 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 (NH_3, 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 (NH_3-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)