UNIVERSITI PUTRA MALAYSIA

MODIFIED SOLID INDUSTRIAL WASTE AS POTENTIAL CATALYST IN PYROLYSIS

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

November 2016

DEDICATION

I dedicate this thesis to my beloved mother Suad Asad…and to my best friend Dr. Abdullah Adnan

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

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Disposal of industrial waste has become a significant environmental issue. Increasing environmental awareness draws attention to find alternative uses to industrial solid waste.

In this work, industrial wastes such as aluminum dross from aluminium recycling process, molten slag from steel manufacturing process and spent oil based mud from petroleum well drilling were treated by physical and chemical methods for potential use in the pyrolysis applications. The industrial wastes were evaluated using state of the arts analysis techniques before and after physical and chemical treatments. The results showed the physical method which representing calcination did not affect much on the properties of the materials like surface area, pore volume, acidity and thermal stability. While the chemical methods were prone to give better properties. Therefore, acid washing method by using hydrochloric acid was chosen as good and economical procedure to improve the activity of the waste material by removing impurities and increasing surface area and acidity of the waste materials for potential catalysts. The surface area and acidity of aluminum dross and spent oil based mud was increased from 0.96 to 68.24 m^2/g and from 315 to 748 µmol/g, from 0.58 to 0.61 m^2/g and from 496 to 1255 µmol/g, respectively. Even though the surface area of molten slag was reduced from 3.4 to 0.85 m^2/g, the acidity was increased from 159 to 1224 µmol/g. The performance of these catalysts was assessed by utilizing them in pyrolysis of waste cooking oil in a fractional system as a feedstock at reaction temperature of 390-420°C with fixed catalyst loading of 5% . The results showed an increase in the yield of the biofuel product produced from the pyrolysis process. Al dross and molten slag were observed to be the best potential catalyst as showed by the gas chromatography analysis. The yield of bio-oil using Al dross as catalyst was 16.43% with 3.2% alkane and 2.5% alkene and the bio-oil using molten slag as catalyst was 14.9% with yield of 18.5% alkanes and 11.76% alkenes and good selectivity in the biofuel range namely C7 to C17.

In conclusion, industrial solid waste after a few modifications, have a potential to be a catalyst in pyrolysis waste cooking oil although they were not showed very significant features in the characterization. All waste materials have a potential as catalysts showing good yield in the catalytic pyrolysis compared to thermal cracking. The product distribution and selectivity obtained from catalytic pyrolysis of waste cooking oil using Al dross and molten slag gave the best performance compared to spent oil based mud-modified catalysts.

Abstrak tesis yang dikemukakan kepada senat Unversiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

PENGUBAHSUAIAN SISA PEPEJAL INDUSTRI SEBAGAI PEMANGKIN BERPONTENSI DALAM PIROLISIS

Oleh

FATEN HAMEED KAMIL

November 2016

Pengerusi	**:**	**Profesor Madya Salmiaton binti Ali, PhD**
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Pelupusan sisa industri telah menjadi satu isu alam sekitar yang sangat ketara. Peningkatan kesedaran terhadap alam sekitar telah menarik perhatian bagi mencari kaedah mudah dan alternatif untuk mengendalikan sisa pepejal perindustrian.

Dalam karya ini, bahan buangan industri seperti hampas aluminium daripada proses kitar semula aluminium, sanga lebur daripada proses pembuatan keluli dan lumpur berasaskan sisa minyak dari penggerudian petroleum, telah dirawat dengan kaedah fizikal dan kimia yang berpotensi digunakan dalam aplikasi pirolisis. Sisa industri telah di analisis menggunakan keadaan teknik analisis seni sebelum dan selepas rawatan fizikal dan kimia. Hasil kajian menunjukkan kaedah fizikal yang mewakili pengkalsinan tidak banyak terjejas terutamanya pada sifat bahan-bahan tersebut seperti luas kawasan permukaan, isi padu liang, keasidan dan kestabilan terma. Selain itu, melalui kaedah kimia yang telah dilakukan, ia memberikan ciri-ciri yang lebih baik. Oleh itu, kaedah pembasuhan asid dengan menggunakan asid hidroklorik telah dipilih sebagai prosedur yang baik dan menjimatkan bagi meningkatkan keaktifan bahan buangan dengan mengeluarkan kekotoran, meningkatkan luas kawasan permukaan dan keasidan bahan-bahan buangan untuk bertindak sebagai pemangkin berpotensi. Kawasan permukaan dan keasidan hampas aluminium dan lumpur berasaskan sisa minyak telah meningkat dari 0.96 kepada 68.24 m^2/g dan dari 315 kepada 748 μmol/g, dari 0.58 kepada 0.61 m^2/g dan dari 496 kepada 1255 μmol/g, masing-masing. Walau bagaimanpun kawasan permukaan sanga lebur telah dikurangkan dari 3.4 kepada 0.85 m^2/g, keasidan meningkat dari 159 kepada 1224 μmol/g. Prestasi pemangkin-pemangkin ini dinilai dengan mengaplikasikan mereka dalam pirolisis sisa minyak masak sebagai bahan mentah di dalam sistem berperingkat pada suhu reaksi 390-420 °C dengan muatan tetap pemangkin sebanyak 5% berat. Hasil kajian menunjukkan peningkatan dalam penghasilan produk bio-bahan api yang dihasilkan daripada proses pirolisis. Hampas Al dan sanga lebur berpotensi untuk menjadi pemangkin terbaik melalui analisis kromatografi gas yang ditunjukkan. Penghasilan bio-minyak dengan menggunakan hampas Al sebagai pemangkin adalah sebanyak 16.43% dengan 3.2% adalah alkana dan 2.5% pula

adalah alkena dan penghasilan bio-minyak menggunakan sanga lebur sebagai pemangkin adalah sebanyak 14.9% dengan hasil sebanyak 18.5% adalah alkana dan 11.76% pula adalah alkena dan pemilihan yang baik dalam kepelbagaian bio-bahan api iaitu C7 ke C17.

Kesimpulannya, sisa pepejal perindustrian selepas beberapa pengubahsuaian, mempunyai potensi untuk menjadi pemangkin dalam pirolisis sisa minyak masak walaupun mereka tidak menunjukkan ciri-ciri yang sangat penting dalam pencirian. Semua bahan buangan mempunyai potensi sebagai pemangkin setelah menunjukkan hasil yang baik dalam pirolisis pemangkin berbanding keretakan haba. Pengagihan produk dan pemilihan yang diperolehi daripada pirolisis pemangkin sisa minyak masak menggunakan hampas Al dan sanga lebur memberikan keputusan yang terbaik berbanding pengubahsuaian pemangkin lumpur berasaskan sisa minyak.

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I certify that a Thesis Examination Committee has met on 21 November 2016 to conduct the final examination of Faten Hameed Kamil on her thesis entitled "Modified Solid Industrial Waste as Potential Catalyst in Pyrolysis" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

Al dross	Aluminium Dross
BET	Brunnauer-Emmett-Teller
BOF	Basic Oxygen Furnace Slag
BFS	Blast Furnace Slag
EAF	Electric Arc Furnace Slag
EDX	Energy-dispersive X-ray spectroscopy
ESR	Electron Spin Resonance Spectroscopy
FA	Fly Ash
FCC	Fluid Catalytic Cracking
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
LF	Ladle Furnace Basic Slag
OBM	Oil-Based Mud
PS	Polystyrene
PET	Polyethylene Terephthalate
PP	Polypropylene
Mt	Million Tons
RCRA	Resource Conservation and Recovery Act
RM	Red Mud
SEM	Scanning Electron Microscopy
TGA	Thermogravimateric Analyzer
TG	Thermogravimateric Curve
TPD	Temperature Programmed Desorption
UV-Vis	Ultraviolet–visible spectroscopy
XRF	X- Ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background of Research

The increasing population, rapid urbanization, the booming economy, and the rise in society's living standards have enormously accelerated the production of industrial solid waste in the world. Thus industrial solid waste has become a global environmental problem. Industrial waste is generated by industrial activities, such as those in factories, mills, and mines. It sometimes remains to be an important part of solid waste. The generation of any waste depletes natural resources, places pressure on land and other resources, such as energy and water, and contaminates the environment. Waste reflects the inability of any modern society and represents lost resources. Industrial processes produce vast amounts of different types of waste materials as byproducts. Most of these wastes are discarded in landfills and contain elements that build up in nature to levels that threaten the future use of natural resources, such as drinking water, agricultural soil, and air, because of the low degradability and toxicity of these wastes (Song et al., 2015). Utilizing these waste products and converting them into valuable materials are wise. The essential motivation in reusing wastes is the direct economic benefits that can be derived and are assigned by diverse cost and price factors because these wastes may contain precious metals and metal oxides. The reuse of wastes plays a significant role in resource protection, is a useful method to save on resources and address pollution, and is a beneficial technique to preserve resources; doing so is an obvious choice that is needed for the protection of society (Xu & Peng, 2009).

Industrial solid wastes contain transition metal oxides compounds, which are used in a vast domain of industrial applications. The oxides of transition metals are highly active in catalytic conversion. Catalysts that depend on these active elements, such as homogenous catalysts, acid mesoporous catalysts, non-acid mesoporous solids, fluid catalytic cracking (FCC) catalysts, zeolites, and metallic oxides, are commercially available (Klose et al., 2000). In addition, metal oxides, such as arsenic, lead, phosphorous, and halogen, are more resistant to poison than noble metals are. The use of industrial wastes containing catalytically active metals, such as iron (Fe), vanadium (V), and nickel (Ni), as alternatives to commercial catalysts can help reduce the cost related to catalyst use (Sushil & Batra, 2008). From the viewpoint of industrial implementation, the use of costly catalysts might condition the economy of the process because high amounts of catalysts are important in the continuous operation of a plant. In conclusion, catalyst cost (type and amount) is a main factor when the economy of both catalytic degradation and thermal degradation is compared (López et al., 2011).

In recent years, studies on the reuse of waste materials have drawn much attention mainly because of both economic and environmental considerations. High volumes of waste materials resulting from large-scale industrial processes afford opportunities in terms of catalysis. A number of catalysts have been reported, and they have been applied in precursors or served as alternative sources in the syntheses of active catalysts. For example, fly ash, a solid residue produced from coal, oil, and biomass combustion, have extensively been investigated for their use as a heterogeneous catalyst, catalyst support, and a feedstock in zeolite synthesis (Kuwahara & Yamashita, 2013). As another example, red mud is a solid residue after caustic digestion of bauxite ores during the production of alumina; it has been applied as a catalyst in hydrogenation, hydrochloronation, and hydrogen oxidation (Liu et al., 2013). Large amounts of waste products allow opportunities for catalysis. The physico-chemical properties of industrial solid wastes depend on the properties of the raw materials involved, their mineralogical origin, the condition of the process, and material performance. The specifications of these wastes, as identified from various processes, show their ability to be used in recycling (Pappu et al., 2007).

Metal oxides have wide applications in different catalytic processes because of their unique properties, such as high surface area, strong active sites, and high concentration of sites. These specifications of metal oxides are likely due to their structure, the type of bond between the metal and oxygen, and the presence of basic and/or acid sites. The properties of catalysts, which contain metal oxides, are due to the adsorption of reactants on unsaturated metal sites and/or oxygen atoms and then the addition or elimination of hydrogen and/or oxygen (Yigezu & Muthukumar, 2014). Many methods are used to improve catalysts and thus obtain high-quality products. The activation process enhances the properties of catalysts, such as their surface area, pore volume, active site, morphology, and thermal stability. Good catalysts can increase the reaction rate, simplify the reaction steps, allow the reaction to occur under mild conditions, and improve selectivity toward the desired products. Furthermore, few raw materials are required, and less unwanted wastes are produced, so certain products that may not be produced without a catalyst can be developed. One of the most important methods to improve the performance of catalysts is calcination. This method is used to enlarge pore volume and increase active sites and thus facilitate ion exchange on the surface of the catalyst. Another method is washing with the use of chemicals. Regardless of the use of acid or alkaline solutions, this type of treatment removes impurities and leaches some metals from the materials. Many types of acids are used for washing, and some examples are HCl, H_2SO_4, and HNO_3. Alkalines such as NaOH and KOH are also used for treatment.

Waste-to-energy is known as a promising alternative to control waste generation and is a possible source of sustainable energy (Tan et al., 2013). One effective method to preserve resources and the environment through the reduction of the amount of nondegradable waste is pyrolysis. Pyrolysis is a chemical decomposition reaction that occurs because of thermal energy in the absence of oxygen (Jahirul et al., 2012). Pyrolysis is useful in converting organic substances into value-added products in the form of liquids, gases, or solids. Regarding the speed of the process, pyrolysis can be categorized as slow, fast, intermediate, or flash pyrolysis (Murugan & Gu, 2015). The cracking process has commonly been achieved with the use of solid catalysts, such as H-ZSM5, Y zeolite, and metal-impregnated MCM-41, which have good shape selectivity and adequate pore size (Lu Li et al., 2014). The production of biofuel from waste cooking oil is competitive and promising. In recent times, the production of biofuel through catalytic cracking methods has increased. Biofuels are in demand because of their similarity in fuel properties with conventional petroleum fuels (Muthukumaran et al., 2015). The presence of catalysts highly alters product distribution. Gas chromatography–mass spectroscopy has been used to examine the chemical composition of oil-selected samples. Fourier transform infrared spectroscopy has been utilized to examine the functional group present, such as alkane, alkene, alcohol, aldehyde, phenols, and ketone in pyrolysis oil (Murugan & Gu, 2015).

Finally, recycling the huge quantities of waste generated in the industrial sector is urgently needed to exploit the use of valuable metal oxides. The utilization of these wastes plays a significant role in resource protection and promotion of a clean environment. Moreover, the commercial catalysts needed to accelerate the reaction are costly, so researchers should find cheap alternative materials to use in the catalytic reactions.

1.2 Industrial solid waste in Malaysia

Aluminum dross, molten slag, and spent oil-based mud are the most important industrial wastes in Malaysia. According to the Ministry of Natural Resources and Environment, the scheduled industrial waste generation in Malaysia in 2010 was 1,880,928.53 metric tons (Brandt & Lim, 2012), and considerable components of this waste were from dross, slag, clinker, ash, gypsum, oil, and hydrocarbon. The amount of aluminum dross, slag, clinker, and fly ash alone in 2010 was 154,223.11 metric tons. In addition, the amount of dross, slag, clinker, and ash have increased to 364,425 metric tons in 2012 (Halimah, 2014). These wastes should be efficiently managed and discarded without causing deleterious environmental effects. In 2009, approximately 126,288 metric tons of industrial wastes were handled by Kualiti Alam Sdn Bhd, Malaysia, and approximately 25,000 tons of bottom ash was produced which were sent to secured landfills. However, disposal by landfilling is an inefficient solution (Naganathan et al., 2012). Despite its huge quantity, industrial solid waste has been given less attention than household waste in research in examining the recycling behavior (Samsudin & Don, 2013).

In Malaysia, the Department of Environment under the Ministry of Natural Resource and Environment defines aluminum dross and molten slag as scheduled waste or waste that needs a license and specific conditions for transport and landfilling in specific areas. Aluminum dross is a waste generated during the aluminum melting process and is a type of solid material floating on molten aluminum (Meor et al., 2009). More than a million tons of aluminum black dross, which is a byproduct of aluminum recycling and a secondary byproduct of the processing of white dross, are generated as landfill materials throughout the world each year. Black dross contains a valuable amount of aluminum oxide (20%–50%) (Tsakiridis et al., 2013). Investigating the use of black dross as a substitute material in other applications is beneficial to exploit all the metal oxides in waste because another resource of aluminum oxide can be explored.

Molten slag is a steel making byproduct, which consists of fused mixtures of metal oxides and silicates. Its highly compressed structure leads to its dense and hard composition. Molten slag is the coarse part of the residues resulting from the separation of molten steel from impurities in the steel manufacturing process (Teoh, 2008). In Malaysia, approximately 750 tons are produced daily, and approximately 7.5 tons of slag produced have been used in various construction activities (Oluwasola et al., 2014). Molten slag is composed primarily of a melted mixture of oxides of iron, silica, calcium, magnesia, and alumina (Shokri et al., 2015). Current practice in handling the molten slag is by recycling parts of the mineral composition as a secondary resource for hydraulic cement and concrete aggregate pavement material in civil engineering work. The remaining parts are disposed of by landfilling and dumping (Kuwahara & Yamashita, 2013). Therefore, researchers are intended to investigate other potential use of molten slag as an abundant and low-cost material in catalytic reaction.

An oil-based mud (OBM) mixture of natural and fabricated chemical compounds is used to cool down and lubricate drill bits, as well as carried cuttings to the surface (Adekunle et al., 2013). The average volume of OBM waste is estimated to be 2000 bbl to 8000 bbl per well (Soegianto et al., 2008). Spent oil-based mud consists of varying concentrations of hydrocarbons and heavy metals. When this material is disposed, it will pollute the environment due to containing heavy metals and hydrocarbons. Spent oil-based mud is commonly disposed of onshore and offshore. Unfortunately, the disposal of industrial wastes in landfills raises the concern that the environmental quality of landfills may be in danger (Khanpour et al., 2014). To address this problem, researchers are investigated alternative methods to treat the used materials through the removal of contaminants (Sayyadnejad et al., 2008).

1.3 Problem statement

Industrial solid wastes are those generated in industrial activities; high production evidently generates a large volume of waste. Most of these industrial wastes contain valuable metals and metal oxides, but these wastes are disposed of and dumped in landfills. This phenomenon has two implications: loss of potential valuable resources since industrial wastes contain a significant amount of materials, and most elements contained in these waste materials may cause hazardous friction when dumping since they cannot be decomposed. Therefore, dumping poses environmental concerns because of its toxic threat. With the increase in environmental awareness, the disposal of any type of hazardous waste has become a significant concern for the industrial sector. In Malaysia, industrial wastes contribute to a considerable amount of the solid waste resulting in from the aluminum industry, the steel production industry, and spent drilling fluid. For years, engineers and chemists have been searching for a possible solution to environmental concerns on waste production and pollution. The challenge for engineers and chemists is to find new methods that minimize material dumping and eliminate the dispersion of harmful chemicals in the environment.

Many researches have been done on industrial solid wastes by utilizing them as alternative sources for metal recovery and these recovered metals are used for catalyst synthesis for other various catalyst applications. However, this method is considered costly and involved many stages. Therefore, a need to find a simple treatment is necessary to manage and at the same time reuse / reprocess the industrial solid waste into value added material.

1.4 Research objectives

This study aims to explore the use of industrial solid wastes in pyrolysis applications. It investigates the usefulness of oil-based mud, aluminum dross, and molten slag as catalysts in the pyrolysis of waste cooking oil in the fractionated cracking system. This study aims to contribute to this growing area of research by exploring the aforementioned catalysts. The specific objectives of the research are as follows:

1. To compare the treatment methods for solid industrial waste modification for potential catalyst by using various analytical instrumentation.
2. To examine the characteristics of the improved high metal oxide wastes as catalysts.
3. To evaluate the improved catalyst performance in pyrolysis of waste cooking oil.

1.5 Scope of work

The scopes of study have been clearly defined to achieve the goal of this research and are listed as follows:

1. Three methods for modifying the industrial solid waste had been used. The first method was thermal activation which it involved exposing the waste materials to high temperature. This method is also known as calcination. Both other methods used chemical activation, one of them involves using HCl for washing the material and then calcination in inert environment. The other one was performed by fusing the material with NaOH in air and after that washing with NH_4Cl followed by calcination the material in inert environment by using N_2.
2. The characterization of waste materials and modified materials were done using Brunnauer-Emmett-Teller (BET) analysis to obtain the surface area and pore volume. X-ray fluorescence (XRF) spectroscopy had been applied to know the chemical composition of materials. The thermal degradation of materials was investigated using the Thermogravimetric analysis (TGA) unit.

The scanning electron microscopy (SEM) produced microscopic images of the samples. Temperature programmed desorption (TPD) determined and evaluated the density and the strength of active site for materials.

3. The method used to test the performance of the materials as catalysts is by applying in pyrolysis of waste cooking oil. Pyrolysis of waste cooking oil was done by fractionated cracking system. The pyrolysis oil produced was characterized using Fourier Transform Infrared Absorption (FTIR) to check the decomposition of carboxylic acid functional group as well as using gas chromatography to determine the quality and the quantity of alkanes and alkenes in the pyrolysis oil.

1.6 Thesis structure

The thesis is organized into five chapters. Chapter 1 presents the introduction, research problem, objectives, and scope of the research. Chapter 2 encompasses reviews on the subject of this research: catalyst and catalysis reaction, industrial wastes, opportunities to use these waste materials as catalysts, catalyst improvement methods, pyrolysis reaction, and pyrolysis waste cooking oil. Chapter 3 describes industrial wastes and the methods used for improving the materials, as well as respective analytical equipment. The pyrolysis application set up (fractionated cracking system) is also described and analytical equipment used for testing bio-fuel. Chapter 4 presents the results and discussions on the obtained results. Chapter 5 concludes the findings and proposes recommendation for future works.

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2. Regeneration of spent transformer oil in electrical stations, First annual scientific conference for General Commission for Research and Industrial Development (2010).
3. Conversion of polyethylene terephthalate waste bottles to terephthalic acid, First annual scientific conference to General Commission for Research and Industrial Development (2010).
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PUBLICATION

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