

SYNTHESIS, CHARACTERIZATION AND
PERFORMANCE STUDY OF CALCIUM OXIDE
CATALYST FROM WASTE EGGSHELL FOR
PYROLYSIS OF EMPTY FRUIT BUNCH

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UNIVERSITI MALAYSIA PERLIS

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PYROLYSIS OF EMPTY FRUIT BUNCH**

by

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LIST OF SYMBOLS

| | |
|-------------------------------|--------------------------------------|
| wt. % | weight percent |
| wt. % / °C | weight percent per degree celsius |
| mg | milligram |
| µm | micrometre |
| cm | centimetre |
| 2θ | two theta |
| mm | millimetre |
| min | minute |
| s | second |
| °C/min | celsius per minute |
| °C/s | celsius per second |
| ml/min | millilitre per minute |
| µl | microlitre |
| MJ/kg | mega joule per kilogram |
| nm | nanometer |
| N | total number of experiments required |
| n | number of independent variables |
| Σ | summation |
| Y | response |
| b ₀ | constant coefficient |
| b _i | linear coefficient |
| b _{ij} | quadratic coefficient |
| x _i x _j | coded values of the factors |
| F- value | test statistic for ANOVA |
| R ² | determination coefficient |
| pred R ² | predicted coefficient |
| Adj R ² | adjusted coefficient |

LIST OF ABBREVIATIONS

| | |
|--------------------------------|--|
| N ₂ | Nitrogen |
| CO ₂ | Carbon dioxide |
| NO _x | Nitrogen oxide |
| SO _x | Sulphur oxide |
| EFB | Empty fruit bunch |
| FFB | Fresh fruit bunch |
| FAO | Food and Agriculture Organization |
| CaO | Calcium oxide |
| CaCO ₃ | Calcium carbonate |
| MgO | Magnesium oxide |
| Fe ₂ O ₃ | Ferric oxide |
| NiO | Nickel oxide |
| ZnO | Zinc oxide |
| TiO ₂ | Titanium dioxide |
| POME | Palm oil mill effluent |
| DTG | Differential thermogravimetric analysis |
| CuO | Copper oxide |
| K ₂ CO ₃ | Pottasium carbonate |
| Ca(OH) ₂ | Calcium hydroxide |
| XRD | X-ray diffractometry |
| JCPDS | Joint Committee on Power Diffraction Standards |
| SEM | Scanning electron microscopy |
| HDPE | High density polyethylene |
| RSM | Response surface methodology |
| CCD | Central composite design |
| PAHs | Polycyclic aromatic hydrocarbon |
| XRF | X-ray fluorescence |
| FTIR | Fourier transform infrared spectroscopy |
| ATR | Attenuated total reflection |

| | |
|--|--|
| EDS | Energy dispersive x-ray spectrometry. |
| HPLC | High performance liquid chromatography |
| ANOVA | Analysis of variance |
| Al ₂ O ₃ | Aluminium oxide |
| SrO | Strontium oxide |
| V ₂ O ₅ | Vanadium (V) oxide |
| CO ₃ O ₄ | Cobalt (II, III) oxide |
| RuO ₂ | Ruthenium (IV) oxide |
| CeO ₂ | Cerium (IV) oxide |
| P ₂ O ₅ | Diphosphorus pentoxide |
| SO ₃ | Sulfur trioxide |
| K ₂ O | Pottasium (II) oxide |
| CO | Carbon monoxide |
| CH ₃ CH ₂ ⁻ , CH ₃ ⁻ , CH ₂ ⁻ | Methyl radicals |

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Kajian Sintesis, Percirian dan Prestasi Pemangkin Kalsium Oksida daripada Sisa-Sisa Kulit Telur untuk Pirolisis Tandan Kosong

ABSTRAK

Pirolisis bermangkin tandan kosong dengan pemangkin sisa kulit telur dijalankan dalam kajian ini untuk mensistesiskan pemangkin kalsium oksida daripada sisa-sisa kulit telur, untuk menyiasat ciri-ciri fizikal dan kimia pemangkin kulit telur dan untuk memberi percirian dan menilai prestasi minyak bio daripada pirolisis bermangkin. Proses pengkalsinan dijalankan di dalam relau bagas bersalur pada suhu 900 °C selama 1 jam untuk penukaran kalsium karbonat kepada kalsium oksida di dalam kulit telur. Komposisi elemen, struktur-struktur kristalit dan struktur morfologikal dilaksanakan untuk percirian kulit telur manakala analisis ultimat dan proksimat, nilai pemanasan dan analisi termogravimetri dijalankan untuk percirian biomas. Pirolisis bermangkin dijalankan dengan pelbagai parameter seperti suhu, kadar pemanasan, masa pegangan dan pemuatan pemangkin untuk mengkaji kesan parameter pirolisis atas hasil minyak. Pengoptimuman dijalankan dengan menggunakan perisian Design Expert 7.1. Hasil minyak dianalisis untuk menentukan kualiti minyak. Minyak paling banyak terhasil pada suhu 400 °C, kadar pemanasan pada 80 °C/min, masa pegangan pada 4 min dan 10% muatan pemangkin. Bagi parameter suhu, hasil minyak meningkat sebanyak 14% sementara hasil gas berkurang sebanyak 13.7% dan hasil arang berkurang sebanyak 0.3%. Bagi parameter kadar pemanasan, hasil minyak dan arang masing-masing meningkat sebanyak 15.4% dan 3.9%, sementara hasil gas berkurang sebanyak 19.3%. Sementara itu, untuk parameter masa pegangan, hasil minyak dan gas masing-masing meningkat sebanyak 10.4% dan 13.1%, sementara hasil arang berkurang sebanyak 23.5%. Hasil minyak dan arang masing-masing telah meningkat sebanyak 14.7% dan 9.6% selepas pertambahan pemangkin telur. Walaubagaimanapun, hasil gas berkurang sebanyak 24.3%. Sementara itu, daripada kajian pengoptimuman, hasil minyak tertinggal diperolehi pada suhu 434.63 °C, kadar pemanasan pada 76.03 °C/min, masa pegangan pada 2.55 min dan 8.02% muatan pemangkin, dengan hasil minyak yang diramalkan adalah 31.81%. Eksperimen pengesahan dijalankan dengan menggunakan keadaan yang sama dan didapati hasil minyak adalah 31.41%. Analisis daripada FTIR dan GCMS menunjukkan kebanyakan komposisi oksigen dan nitrogen berkurang selepas pertambahan pemangkin seperti komposisi asid karboksilik, amida, amina dan keton sementara hidrokarbon dan fenol telah meningkat.

Synthesis, Characterization and Performance Study of Calcium Oxide Catalyst from Waste Eggshells for Pyrolysis of Empty Fruit Bunch

ABSTRACT

Catalytic pyrolysis of empty fruit bunch with eggshell waste catalyst were conducted in this studied to synthesized calcium oxide catalyst from waste eggshell, to investigate the physical and chemical properties of calcium oxide catalyst, and to characterize and evaluate the performance of bio-oil from catalytic pyrolysis. Calcination process was conducted in tube furnace at temperature of 900 °C for 1 hour for converting the calcium carbonate to CaO in the eggshell. Elemental composition, crystallite structures, and morphological structures were performed for characterization of eggshell while ultimate and proximate analysis, heating value, and thermogravimetric analysis was performed for characterization of biomass. Catalytic pyrolysis was conducted by different parameters such as temperature, heating rate, holding time and catalyst loading to study the effect of pyrolysis parameters on oil yield. Optimization was performed by Design Expert 7.1 Software. Oil yield were analyzed in order to determine the quality of oil. High oil yield were obtained at temperature of 400 °C, heating rate of 80 °C/min, holding time at 4 min and 10% of catalyst loading. For temperature parameter, oil yield was increased by 14%, while gas yield reduced by 13.7% and char yield reduced by 0.3%. For heating rate, oil and char yield was increased by 15.4% and 3.9%, respectively, while gas yield decreased by 19.3%. Meanwhile, for holding time parameter, the oil and gas yield was increased by 10.4% and 13.1%, respectively while char yield decreased by 23.5%. The oil and char yield increased by 14.7% and 9.6%, respectively after the addition of eggshell catalyst. However, gas yield reduced by 24.3%. Meanwhile, from optimization studied, high oil yield were obtained at temperature of 434.63 °C, heating rate of 76.03 °C/min, holding time at 2.55 min, and 8.02% of catalyst loading, with predicted bio-oil yield was 31.81%. Confirmation runs were performed by using the same conditions and gave an average of 31.41%. Analysis from FTIR and GCMS showed that most of oxygenated and nitrogen compound were reduced after the addition of catalyst such as carboxylic acids, amide, amines and ketones compound while hydrocarbon and phenols were increased.

CHAPTER 1

INTRODUCTION

1.7 Background of research

Energy source is one basic needed in this modern life. As the development of modern civilization, the uses of energy sources have become increase. Fossil fuels are one of the energy resources and the demanding of the energy sources nowadays lead to decrease in fossil fuels. The production of fossil fuels has reached up to 79% compared to the other energy sources (Nasir et al., 2013). Furthermore, the uses of fossil fuels may contribute to increase in emissions of greenhouse gases such as CO₂, NO_x, and SO_x, which led to global warming. Thus, alternative ways are being search to alternate the non-renewable energy to the renewable energy. Renewable energy sources are clean, low risk, and inexhaustible (Dincer, 2001 and Bilgen et al., 2004). Renewable energy sources included geothermal, hydropower, solar, wind and biomass. Biomass energy is the most compatible energy sources as it is one of the renewable energy. Biomass is known as sustainable, renewable, and green sources of energy.

Biomass energy has same potential with the energy from fossil fuel as it can be stored, renewed, and transferred (Halder et al., 2014). Energy from the biomass resource gives many advantages towards the green energy such as vaster resource capacity, less sulfur composition, less ash content, have lower price and one of the feature of renewability (Halder et al., 2014). With the use of available science and technology,

some advanced techniques, with development of new energy conversion methods, biomass resources would be more efficient in order to meet the future energy demand.

Some alternative methods for conversion of biomass to energy have been introduced in this recent years which are biological and non-biological process. Biological process includes fermentation process and anaerobic digestion, where bacteria was used to degrade the biomass into an energy. In contrast with the biological process, non-biological process mainly thermal conversion process. However, high cost of production obtained when using biological process. Hence, thermal conversion process is getting more attention as it has potential to generate energy in a large scale and economical. There are three process under thermal conversion process which are combustion, gasification, and pyrolysis. Combustion is the process of chemical reactions between fuel and oxidant by producing heat.

On the other hand, gasification is a process for converting organic or fossil fuels based carbonaceous material to carbon monoxide, hydrogen, and carbon dioxide gaseous with high temperature with controlled amount of oxygen. Pyrolysis is thermochemical decomposition of organic material in the absence of oxygen. Pyrolysis gain more attention in conversion of energy from biomass and the products from this process included solid, liquid, and gas. Those products can be used directly, or can be further treatment for secondary products. Bio-oil was produce in this pyrolysis process have benefits in various static applications such as boilers and furnace (Bridgwater and Peacocke, 2000). However, low pH of oil product is due to the present of organic acids, thus increasing corrosion and storage issues. To overcome this issue, bio-oil can be upgraded by removing unwanted compound such as oxygen. To accomplish these result, biomass can be pyrolyzed in the presence of catalyst in order to increase the volume and features of oil product.

1.2 Generation of empty fruit bunch in Malaysia

The Malaysian palm oil industry is leading in technology and production for the global markets. Palm oil and related products represent the second largest export of Malaysia in the first nine months of 2005 (Sulaiman and Abdullah, 2011). The greatest production of palm oil also generate their residues. Malaysia generate residues from their oil palm plantations include empty fruit bunch (EFB), trunks, fronds, palm fibre, and palm kernel shell. Table 1.1 shows the typical product stream distribution in oil palm mills. 4.42 tonnes per hectare of EFB is produced from wet fresh fruit bunch (FFB), while from dry FFB, it generates about 1.55 tonnes per hectare of EFB. EFB from oil palm is a major solid waste in the oil palm industry besides kernel and shells. The abundance of EFB waste contribute to the environmental problem as it has no value.

Table 1.1. Typical product stream distribution in oil palm mills (Source: Yusoff, 2006).

| | Wet FFB basis | | Dry FFB basis | |
|--------------------|----------------------|-------|----------------------|-------|
| | (tonnes per hectare) | % FFB | (tonnes per hectare) | % FFB |
| FFB | 20.08 | 100 | 10.6 | 100 |
| Palm oil | 4.42 | 22 | 4.42 | 41.7 |
| Palm kernel | 1.2 | 6 | 1.2 | 11.4 |
| EFB | 4.42 | 22 | 1.55 | 14.6 |
| POME | 13.45 | 67 | 0.67 | 6.3 |
| Shell | 1.1 | 5.5 | 1.1 | 10.4 |
| Fibre | 2.71 | 13.5 | 1.63 | 15.4 |
| Total | 27.3 | 136 | 10.6 | 99.7 |

EcoIdeal and Mesilin (2006) observes that waste from palm oil mill in the condition of biomass residue such as EFB can be a potential renewable energy producer in Malaysia. It can help to reduce global warming by displacing the use of fossil fuels (McKendry, 2002 and Li et al., 2009). In reducing emissions of greenhouse gases, EFB is used to control weeds, prevent erosion, and maintaining soil structures. However, this kind of methods increase the processing cost for transportation and hiring the labour for work. Thus, others alternative way have been introduced to reduce air pollution such as pyrolysis. Pyrolysis process give many advantages especially in the environment point of view, where the production of gases have a desirable properties for energy production, pyrolysis oil, and solid char which are the three products are useful in the industry.

1.3 Eggshell as calcium oxide (CaO) catalyst

Egg is a major ingredient in variety of product such as cakes, fast food, and also in daily meal. The production of chicken eggs in the industrial lead to generate it shells, which are considered as waste. A part from that, waste eggshell have no economic value and most of it have been discarded to the landfill without any processing. This could be an important issue, which can cause high risk to public health and polluting the environment. High generation of waste eggshell may increase the production of solid waste in the landfill as eggshell is part of the solid waste.

About 642 600 tonnes of egg production in Malaysia in the year of 2012 (FAO, 2014). 11% of the total weight is denoted by the shell which can be estimated about 70 686 tonnes for waste generated per year (Soares et al., 2013). The percentage of waste eggshell generation is expected to be increased year by year and this will cause environmental issue. Eggshells contain calcium carbonate (CaCO_3) which is main

element in the eggshell. About 94% of CaCO_3 , 1% of magnesium carbonate, 1% of calcium phosphate, and 4% of organic matter contain in the eggshell (Lunge et al., 2012). CaCO_3 can be converted to calcium oxide (CaO) via calcination process. CaO was the active phase in the eggshells which can resulting high result in the oil production and suitable temperature for calcination process must be above 800°C (Wei et al., 2009).

Thus, waste eggshell is expected to be a source of this substance as it has low cost of production, non-corrosive, and environmental friendly product. CaO from waste eggshell is expected to replace others commercial calcium oxide that are more expensive and high cost of production. To address these issues, an alternative way had been studied to characterize potential mineral such as CaO from eggshells. CaO from eggshell is expected to be a catalyst for bio-oil production as it can reduce oxygen content, which is unnecessary compound in the production of bio-oil via catalytic pyrolysis. The presence of oxygen in the bio-oil give negatively affect such as further increasing corrosion due to its low pH. Lu et al., (2010) reported that CaO reduced heavy products such as phenol and increased formation of hydrocarbons and light product such as acetaldehyde, 2-butanone, and methanol. CaO also can reduce acid. Other catalyst including MgO , Fe_2O_3 , NiO , ZnO and TiO_2 were not effective as CaO . Hence, CaO is a suitable catalyst for enhancing the quality of bio-oil.

1.4 Problem statement

Catalytic pyrolysis of biomass with zeolite and mesoporous catalysts produce low yield of bio-oil and high content of carboxylic acids. Thus, alkaline earth metal oxide catalysts such as CaO is expected to increase the bio-oil yield. CaO is a raw material for producing lime in the industry (Oliveira et al., 2013). Using CaO from lime

stone may contribute to environmental problem as source of this commercial CaO is non-renewable resource. Large usage of non-renewable CaO caused rapid depletion of those resources. Hence, it would increase the cost of oil production. The huge amount of waste eggshell that was discharged could be a resource of the catalyst for pyrolysis process. CaO from waste eggshells not only gives an opportunity to use it as a catalyst but also adds value to the waste generated.

1.5 Scope of research

This research is conducted to study the catalytic pyrolysis of EFB as biomass and waste eggshell as catalyst. Waste eggshell which contain most of CaCO_3 are calcined to CaO before mixing with the EFB. Bio-oil, by-product of the thermochemical conversion process is then characterized to see the quality and potential renewable energy product.

1.6 Objectives

1.6.1 To synthesis and investigate the chemical and physical properties of calcium oxide catalyst from waste eggshell.

1.6.2 To characterize and evaluate the performance of bio-oil from catalytic pyrolysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The energy utilization from biomass resources have received much attention. Pyrolysis is a method to produce energy. Catalytic pyrolysis consists of thermal degradation of biomass with the help by the catalyst. Pyrolysis of biomass with the catalyst would increase the production of bio-oil, in fact the oil yield have a good quality for conventional uses. Biomass and catalyst characterization, catalytic pyrolysis, effect of pyrolysis parameter on product yields, pyrolysis products and optimization of pyrolysis condition were discussed in this chapter.

2.2 Biomass resources

Biomass is organic matter derived from the living organisms or living things. In the context of energy from biomass, this is usually used to mean plant based material, but biomass can apply for both animal and vegetable derived materials (Panwar et al., 2012 & Saxena et al., 2009). Biomass can include wide range of materials such as wood from forestry or wood processing, agriculture harvesting and processing, agricultural residues, industrial waste, food waste, domestic and municipal waste, and animal manure. It can substitute fossil fuels as it can be a natural and renewable resource based

on carbon. Biomass also is renewable in the sense that only a short period of time is needed to replace what is used as an energy resource (Balat and Ayar, 2005 & Klass, 2004). At present, the palm oil industry produce large quantity of biomass from the oil extraction process such as empty fruit bunch (EFB), palm oil mill effluent (POME), mesocarp fiber, and shell. Fig 2.1 showed the trend of production of oil palm in Malaysia from 2004 until 2009 in million tonnes. It can be seen that the production have increased from the year 2007 to 2009.

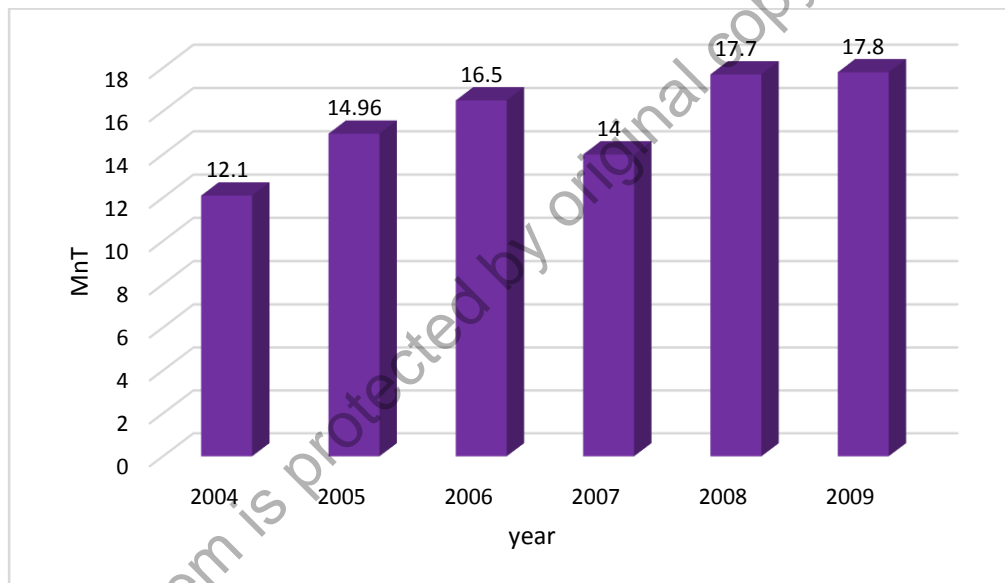


Figure 2.1. Palm oil production in Malaysia from 2004 to 2009 (Mohammed et al., 2011).

2.2.1 Characterization of biomass

The chemical and physical properties of biomass are different according to their diverse origins and plant species. The major organic components and chemical structure in biomass were very substantial in the progress of processes to produce derived chemicals and fuels. Primarily, biomass comprises of carbon, hydrogen, nitrogen and