



**DEVELOPMENT OF CARBON-INFILTRATED
BIOCHAR USING OIL PALM EMPTY FRUIT BUNCH
AS AN ALTERNATIVE SOURCE OF ENERGY**

BY

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ABSTRACT

Fossil fuels have been the main energy source worldwide, and they are facing serious depletion. Production of cokes from coals requires extensive energy and releases high amount of CO₂ which leads to environmental deterioration. As one of alternatives to fossil fuels, oil palm empty fruit bunch (OPEFB) has been generated abundantly in Malaysia, but the utilization is still in a small scale due to the fact that this biomass contains more than 50% moisture, which makes it less efficient when it comes to solid biofuel production. This research presents a developed process to produce an upgraded value of OPEFB-derived biochar, namely carbon-infiltrated biochar, by integrating pyrolysis and tar decomposition processes using chemical vapor infiltration (CVI) method. In the first part of the study, OPEFB was heated slowly in an inert atmosphere to produce biochar before carbon deposition was carried out. The terminal temperature was 500°C with 10°C/min produced 78 mass% carbon content of biochar. Integrated fast pyrolysis-tar carbonization process done at 450°C with 60°C/min resulted in 5.2 mass% carbon increase. Crushing strength of these carbon-infiltrated biochar was also increased. In the second part, the biochar produced at the optimized temperature and heating rate was used as a substrate for tar decomposition to take place and for solid carbon to deposit on its pore surface. Tar source was OPEFB particles which were heated rapidly at heating rates of more than 100°C/min to produce a large amount of tar vapor containing high carbon yield. The CVI method causes tar decomposition into gases and solid carbon where the latter was loaded into porous biochar substrate to increase the carbon content and its calorific value so that it can be utilized as an alternative energy source. The product obtained was carbon-infiltrated biochar containing increased carbon content up to 6.1 mass % and consequently achieved an increased calorific value up to 26.0 MJ/kg – suitable to be used as an alternative energy source. The mechanism of carbon deposition within porous biochar was also discussed. The overall evaluation of the proposed system was carried out on the basis of its exergetic performance to confirm the advantages of the developed process system, and 41% of exergy loss was able to be achieved in comparison with the conventional system.

الملخص

أصبح الوقود الأحفوري مصدراً رئيسياً للطاقة في أنحاء العالم، مما أدى إلى استنزافه بشكل كبير. كما أن إنتاج فحم الكوك من الفحم الحجري يستهلك طاقة كبيرة ويُنتج كمية كبيرة من غاز ثنائي أكسيد الكربون الذي يفسد البيئة. أحد بدائل الوقود الأحفوري التي تنتج بكثرة في ماليزيا هي عناقيد فاكهة زيت النخيل الفارغة (OPEFB). ولكن استخدامها لا يزال في نطاق ضيق بسبب احتواء هذه الكتلة على أكثر من 50% من المادة الرطبة مما يجعلها أقل كفاءة عندما يتعلق الأمر بإنتاج الوقود الحيوي الصلب. يقدم هذا البحث طريقة متطورة لإنتاج قيمة مطورة من الفحم النباتي المشتق من (OPEFB) والمسمى الفحم النباتي متصلل الكربون، وذلك من خلال دمج عمليات الانحلال الحراري والتحلل القطراني باستخدام أسلوب تسلل الأبخرة الكيميائية (CVI). في الجزء الأول من الدراسة، تم تسخين عناقيد فاكهة زيت النخيل الفارغة (OPEFB) ببطء في بيئة خاملة لإنتاج الفحم النباتي قبل إجراء ترسيب الكربون. بلغت درجة الحرارة النهائية 500 درجة سيليزية بمعدل ارتفاع حراري قدره 10 درجة سيليزية/دقيقة أنتجت كتلة من الفحم الحجري تحوي 78% كربون. أدى التسريع المتكامل لعملية التفحيم بالانحلال الحراري للقطران بدرجة 450 سيليزي بزيادة 60 درجة سيليزية/دقيقة إلى زيادة 5.2% في كتلة الكربون وكذلك زيادة قوة سحق الفحم النباتي متصلل الكربون. في الجزء الثاني من الدراسة، تم إنتاج الفحم النباتي في درجة الحرارة ومعدل ارتفاع الحرارة الأمثل باعتبارهما ركيزة حدوث تحلل القطران، وكذلك لعزل الكربون الصلب على سطح مساماته. استخدمت جزيئات (OPEFB) كمصدر للقطران حيث تم تسخينها بمعدل سريع قدره 100 درجة سيليزية/دقيقة لإنتاج كمية أكبر من بخار القطران التي تحتوي على كمية كربون عالية. أدى أسلوب (CVI) إلى تحلل القطران إلى غازات وكربون صلب حيث تم تعبئة هذا الأخير في مسامات الفحم النباتي التحتية لزيادة محتوى الكربون وقيمه الحرارية ليتم استخدامه كمصدر للطاقة البديلة. المنتج المستخرج هو الفحم النباتي متصلل الكربون الذي يحوي على كمية أكبر من الكربون تصل إلى 6.1% كتلة وبالتالي حققت قيمة زيادة حرارية تصل إلى 26.0 ميغا جول/كغ المناسبة لاستخدامها كمصدر للطاقة البديلة. كما تمت مناقشة آلية ترسيب الكربون في مسامات الفحم النباتي. التقييم النهائي لأداء النظام المقترح تم بالاعتماد على أداء الطاقة المتاحة لتأكيد مزايا نظام العملية المتطور، حيث حقق انخفاضاً قدره 41% في الطاقة المتاحة بالمقارنة مع النظام التقليدي.

APPROVAL PAGE

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DECLARATION

I hereby declare that this thesis is the result of my own investigations except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at International Islamic University Malaysia or other institutions.

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LIST OF ABBREVIATIONS

a-C	Amorphous Carbon
BHA	Butylated Hydroxyanisole
Bt	Billion tonnes
B-S	Broido-Shafizadeh
CHNO	Carbon, Hydrogen, Nitrogen, Oxygen
C-I	Carbon-Infiltrated
COG	Coke Oven Gas
CVI	Chemical Vapor Infiltration
D peak	Defect of Disorder peak
DA	Dubin-Astakhov
d.a.f.	Dry Ash-Free Basis
d.b.	Dry Basis
EFB	Empty Fruit Bunch
EXL	Exergy Loss
FE-SEM	Field Scanning Electron Microscopy
FFB	Fresh Fruit Bunch
G peak	Graphite peak
GC	Gas Chromatography
HEX	Heat Exchanger
H.C.	Heavy Hydrocarbons
HHV	Higher Heating Value
La	Cluster Diameter
L.C.	Light Hydrocarbons
Mt	Million tonnes
OPEFB	Oil Palm Empty Fruit Bunch
PG	Propyl Gallate
PKS	Palm Kernel Shell
PMF	Palm Mesocarp Fiber
POME	Palm Oil Mill Effluent
R/P	Reserve to Production Ratio
SEM	Scanning Electron Microscopy
ta-C	Tetrahedral Amorphous Carbon
TBHQ	Tert-Butylhydroquinone
T.C.	Thermocouples
TGA	Thermogravimetry Analysis

LIST OF SYMBOLS

ϵ_C	Chemical Exergy
ϵ_{in}	Exergies of input materials
ϵ_{out}	Exergies of output materials
ϵ	Exergy
ω_G	Graphitic peak position
<	Less than
ϵ_M	Mixing Exergy
>	More than
%	Percent
ϵ_P	Pressure Exergy
ϵ_T	Thermal Exergy

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

1.1.1 Renewable Energy Source

At present, fossil fuels have been the main energy source worldwide, and with the increasing trend of world energy consumption, utilization of efficient alternative energies is highly demanded. These alternatives include renewable energy sources and one of the aims of these alternative energies is to reduce the extensive utilization of the non-renewable energy sources which is now facing depletion and causing environmental pollutions. One of the attractive renewable energy sources is from biomass. Biomass consists of primarily carbon, hydrogen and oxygen, and approximately 146 billion metric tons are produced per year worldwide (Balat and Ayar, 2005).

Malaysia is one of the largest palm oil producers and the palm industry continuously generates plenty of biomass residues. For every kilogram of palm oil obtained, 4 kilograms of dry solid palm residues are generated, and in 2010 alone, 80 million dry tons of solid waste in Malaysia was produced from this palm industry. This figure is expected to grow to 100 million dry tons by 2020 (Agensi Inovasi Malaysia, 2011). Solid palm residues include palm kernel shell (PKS), palm mesocarp fiber (PMF) and oil palm empty fruit bunch (EFB/OPEFB). Most of the solid waste generated is OPEFB – the leftovers after palm fruits are collected from fresh fruit

bunch, harvested from palm trees for the oil. PKS has been utilized as fuels for electricity generation in milling process at the plantation but OPEFB is underutilized - merely being composted as a fertilizer or used for mulching (Ali et al., 2013). Plenty of the OPEFB is being dumped in landfills because of the regular large production of palm oil, and this has created an environmental problem due to the lack of efficiency in waste management (Golder Associates, 2006).

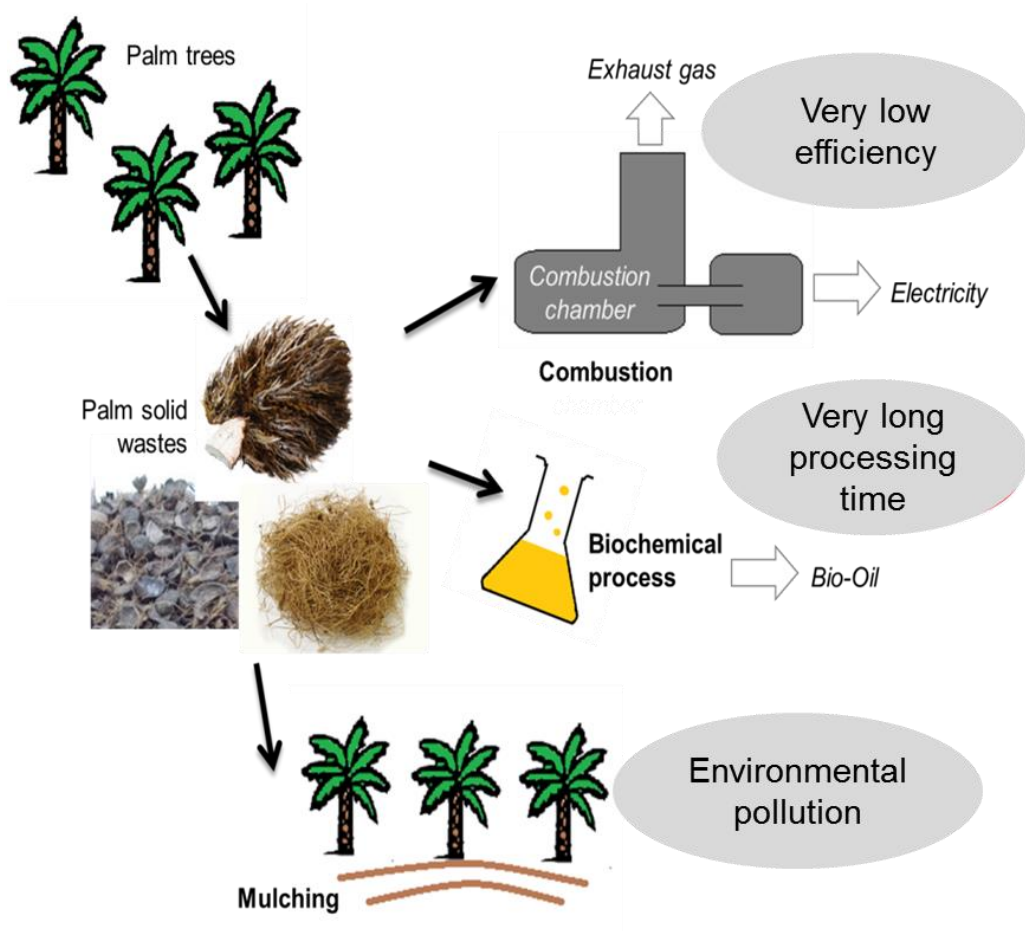


Figure 1.1: Current practise and utilization of palm oil industry solid wastes.
**Note: Starting from 2013, enforcement was made by Malaysian government to ban direct combustion of OPEFB at palm oil mills.*

1.1.2 Utilization of biomass

The conversion of biomass to energy includes thermochemical and biochemical processes. Thermochemical process includes pyrolysis, gasification and combustion (Jackson and Lofsedt, 1998). Pyrolysis is performed at an absence of oxygen at low temperatures, around 350 to 700°C, where its main products are bio-oil and biochar. On the other hand, gasification process requires an atmosphere of insufficient oxygen and it is carried out at higher temperatures, typically at temperatures more than 700°C and up to 1200°C. The main product of complete gasification is syngas (CO and H₂) to be used for heating or generation of electricity. Combustion is conducted with the presence of oxygen at temperatures higher than those of gasification process to produce steam for heating purposes (Ciubota-Rosie, Gavrilesu and Macoveanu, 2008). Table 1.1 presents the differences of these thermochemical processes (Shafizadeh and Lai, 1972; Koufopoulos, 1991; Brown, R. C., 2011).

Table 1.1: Thermochemical processes and the respective main products

Process	Atmosphere	Temperature (°C)	Main Product
Slow Pyrolysis	Inert	350-500	Biochar
Fast Pyrolysis	Inert	500-700	Bio-Oil / Tar vapour
Gasification	Insufficient oxygen / Steam	800-1200	CO, H ₂ , CO ₂ , CH ₄ , H ₂ O, Hydrocarbons
Combustion	Air	>1200	CO ₂ , H ₂ O

Oil palm solid wastes are mostly being utilized within the palm plantation, where they are used for mulching and some are combusted for power generation (Figure 1.1). Direct biomass combustion has been a traditional way of using biomass, where the biomass is completely transformed into heat. Nevertheless, direct combustion of biomass for power generation was reported to have only 8-12% thermal efficiency due to this problem (Xie et al., 2013). In addition, since early 2013, enforcement has been made by Malaysian government to ban combustion of OPEFB at palm oil mills to generate electricity due to the air pollution it has caused. Besides, by using this disposal method, it was claimed that no energy was able to be recovered (Abdullah and Sulaiman, 2014). Biochemical process is also implemented to obtain bio-oil from these palm oil industry solid wastes. However, these processes cause environmental pollution and energy wastage. Therefore, it is an attractive proposition to find alternative ways to utilize these wastes.

Utilization of biomass has a high potential to substitute coal because it has been regarded as a carbon-neutral fuel when burned (Du et al., 2014). However, when compared to coal, biomass has lower energy density and carbon content, and higher moisture content (Rousset et al., 2011), which makes biomass utilization less energy efficient in industries. Therefore, it is more preferable to convert biomass into products that have increased calorific values before utilizing them as a more effective fuel. This also promises advantages such as transportation, storage, and flexibility in production and marketing.

1.1.3 Pyrolysis of biomass

One of the most prominent methods to use biomass for fuel is by pyrolysis, a thermochemical process. Pyrolysis produces useful fuel gases, biochar and biotar. Fuel gases from this process can be used directly as an energy source. Biochar is a carbonaceous material normally used in agricultural industry in soil amendment because of its porous characteristic which makes it able to trap impurities excellently (Zhang et al., 2012; Galinato, Yoder and Granatstein, 2011; Ducey et al., 2013; Wang et al., 2012; Yu et al., 2011). Biotar from biomass pyrolysis has been a serious issue because it clogs fuel lines, filters, and engines, thus reducing the efficiency of biomass utilization (Mermelstein, Millan and Brandon, 2011). Even so, biotar contains a mixture of naturally occurring compounds, including carbon, which makes it attractive to be collected and used as a fuel source. In the pyrolysis of biomass, different treatment parameters give significant differences in the product yields. Manipulation of the pyrolysis conditions can potentially add value to the biomass itself and may contribute significantly to the bio-based economy that is compatible with the environment.

In biofuel production from mass, the gas produced by biomass pyrolysis and/or gasification is beneficial as a fuel since it can be directly recycled, whereas biochar needs to meet certain criteria and specifications in order to be able to be used as a solid biofuel in particular applications, with carbon content and calorific values being the most important characteristics for a biofuel. Biotar generally contains highly condensable hydrocarbons, which needs to be removed by decomposing it into gases by gasification process at high temperatures.

1.1.4 Oil Palm Empty Fruit Bunch (OPEFB)

Generally, OPEFB contains more than 50% moisture, and sometimes the moisture content may reach up to 65%. Due to this reason, most researchers opt to produce fuel in the form of bio-oil from OPEFB. However, during bio-oil production, an unwanted secondary reaction often takes place to decompose biotar vapour into secondary char and gases. This reaction is very difficult to avoid, and if is not minimized, it will reduce the heating value of the resulting bio-oil product because the carbon content has changed into the secondary char in solid form. On the other hand, if a solid biofuel is of interest, an OPEFB-derived biochar is not an optimal option since it normally does not have enough carbon and heating values – two important characteristics – to be a good biofuel. Besides that, the amount of thermal energy required to remove the moisture alone is very large.

Consequently, an OPEFB-derived biochar needs to be upgraded for OPEFB to be efficiently converted into solid biofuel. With this in mind, the upgraded product is anticipated to help minimize the consumption of fossil fuels, as well as to lower the CO₂ emissions from fossil fuels.

1.1.5 Fossil fuels and CO₂ emission

Coal, petroleum and natural gas are three main fossil fuels available throughout the world and they are currently facing depletion due to its non-renewable consumption to accommodate human and industrial needs. Coal recorded an increase of 3% consumption in 2013 – the fastest-growing fossil fuel consumption. Global primary

energy consumption depicted coal's share to reach 30.1%, the highest ever recorded since 1970.

The ratio of reserves to production, R/P, of coal (Figure 1.2) was calculated for North America, South and Central America, Europe and Eurasia, Middle East and Africa, Asia Pacific, and for worldwide. A higher R/P ratio indicates a longer time for these regions to sustain their coal productions. The overall R/P ratio of coal worldwide is 113, with Europe and Eurasia region had the highest R/P ratio, 254, as compared to other regions. North America had the second highest R/P ratio followed by the South and Central America whereby Asia Pacific region recorded the lowest R/P ratio. The 2013 R/P ratio for this region is presented in Figure 1.3. The R/P ratio for Japan exceeds all other countries in the same region, followed by Australia and New Zealand.

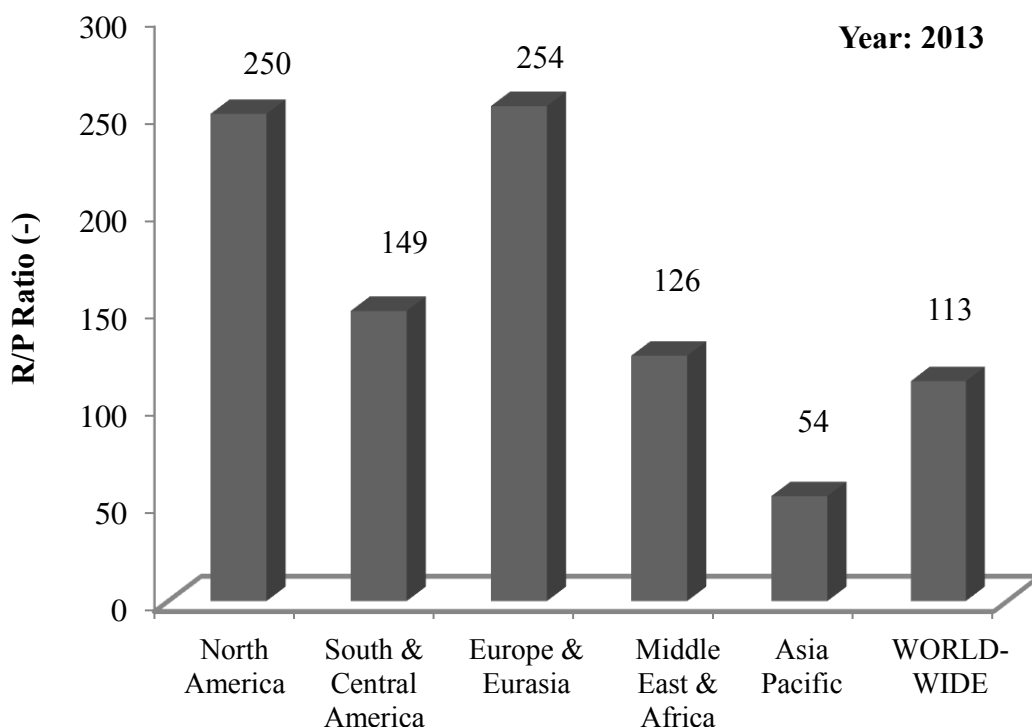


Figure 1.2: Reserve to production ratio (R/P) of coal (BP Statistical Review of World Energy, 2014)