# PREPARATION OF SOLID BIOFUEL DERIVED FROM PALM KERNEL SHELL WASTE VIA PYROLYSIS AND HYDROGENATION PROCESS

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# ABSTRACT

The need for energy is always expanding along with industrialization and population increase, and the availability of energy supplies cannot keep up with the mounting consumption. In 2000, one estimate predicted that about 20 million metric tons of $CO_2$ will be released into the atmosphere yearly. While this pattern continues, extreme natural catastrophes, such as excessive rainfall and the ensuing floods, droughts, and local imbalance, are to be expected. The world's oil reserves are expected to run out by 2050. Considering the mentioned aspects there has been an elevating demand for renewable resources of energies. One of such mentionable sources of energy is palm oil leftovers or palm kernel shells (PKS). Low moisture content, compact and having a high calorific content are some of the mentionable factors contributing to the popularity of PKS. Considering the mentioned aspects, in this study, the potential of palm kernel shell waste as a solid biofuel by using pyrolysis and hydrogenation process has been evaluated along with analysing the impact of temperature in achieving a higher calorific value. In order to evaluate the heating values of the samples, Bomb calorimeter has been used and TGA analysis has been performed to evaluate the impact of temperature and associated changes in the weight of the sample. For analysing the compound group present in the samples, FTIR analysis has been conducted. The highest heating value of 25.96 MJ/kg was obtained for sample prepared at 300$^{o}$C hydrogenation temperature at 1 hour with the use Ru/Mn/ce-65 as catalyst. Significant C-H stretching and vibration was observed at 2850 – 3000 cm$^{-1}$ and 1120-1250 cm$^{-1}$ wavelength which indicate increasing C-H adsorption at carbon surface that become a major contribution to higher heating value. In addition to that, temperature has been observed to have major impact on the performance of the samples in attaining higher calorific value as compared to reaction time. Therefore, PKS proved to have a great potential as green waste to be used as a high-quality solid biofuel for combustion purposes.

# ABSTRAK

Keperluan untuk tenaga sentiasa berkembang seiring dengan perindustrian dan pertambahan penduduk, dan ketersediaan bekalan tenaga tidak dapat bersaing dengan penggunaan yang semakin meningkat. Pada tahun 2000, satu anggaran meramalkan bahawa kira-kira 20 juta tan metrik $CO_2$ akan dibebaskan ke atmosfera setiap tahun. Walaupun corak ini berterusan, malapetaka semula jadi yang melampau, seperti hujan yang berlebihan dan banjir, kemarau dan ketidakseimbangan setempat, adalah dijangkakan. Rizab minyak dunia dijangka akan kehabisan menjelang 2050. Memandangkan aspek-aspek yang disebutkan, terdapat permintaan yang meningkat untuk sumber tenaga boleh diperbaharui. Salah satu sumber tenaga yang boleh disebut ialah sisa minyak sawit atau cangkerang isirong sawit (PKS). Kandungan lembapan yang rendah, padat dan mempunyai kandungan kalori yang tinggi adalah antara faktor yang boleh disebut menyumbang kepada populariti PKS. Dengan mengambil kira aspek-aspek yang dinyatakan, dalam kajian ini, potensi penggunaan sisa tempurung isirong sawit sebagai biobahan api pepejal dengan menggunakan pirolisis dan penghidrogenan telah dinilai bersama-sama dengan menganalisis kesan suhu dalam mencapai nilai kalori yang lebih tinggi. Untuk menilai nilai pemanasan sampel, kalorimeter Bom telah digunakan dan analisis TGA telah dilakukan untuk menilai kesan suhu dan perubahan yang berkaitan dalam berat sampel. Untuk menganalisis kumpulan kompaun yang terdapat dalam sampel, analisis FTIR telah dijalankan. Nilai pemanasan tertinggi iaitu 25.96 MJ/kg diperolehi bagi sampel yang disediakan pada suhu penghidrogenan 300$^{o}$C pada 1 jam dengan menggunakan Ru/Mn/ce-65 sebagai mangkin. Regangan dan getaran C-H yang ketara diperhatikan pada 2850 – 3000 $cm^{-1}$ dan 1120-1250 $cm^{-1}$ panjang gelombang yang menunjukkan peningkatan penjerapan C-H pada permukaan karbon yang menjadi sumbangan utama kepada nilai pemanasan yang lebih tinggi. Di samping itu, suhu telah diperhatikan mempunyai kesan besar ke atas prestasi sampel dalam mencapai nilai kalori yang lebih tinggi berbanding dengan masa tindak balas. Oleh itu, PKS terbukti mempunyai potensi besar sebagai sisa hijau untuk digunakan sebagai biofuel pepejal berkualiti tinggi untuk tujuan pembakaran.

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| AC | - | Activated Carbon |
| ASTM | - | America Society for Testing and Material |
| CDM | - | Clean Development Mechanism |
| CHP | - | Combined Heat and Power |
| CoP | - | Conference of Parties |
| CPKS | - | Char Palm Kernel Shell |
| CV | - | Calorific Value |
| DAF | - | Dry Ash Free |
| DTG | - | Derivative Thermogrametric |
| EFB | - | Dry Fruit Bunch |
| FTIR | - | Fourier Transform Infrared Spectroscopy |
| GHG | - | Greenhouse Gases |
| HCPKS | - | Hydrogenated Catalytic Palm Kernel Shell charcoal |
| HT | - | Hydrothermal Treatment |
| HTC | - | Hydrothermal Treatment Carbonization |
| HWCPKS | - | Hydrogenated Without Catalyst Palm Kernel Shell charcoal |
| LC | - | Lignite Char |
| MF | - | Mesocarp Fruit Fibre |
| OCED | - | Organisation for Economic Co-operation and Development |
| OPF | - | Oil Palm Frond |
| OPT | - | Oil Palm Trunk |
| PKS | - | Palm Kernel Shell |
| POME | - | Palm Oil Mill Effluent |
| RPKS | - | Raw Palm Kernel Shell |
| TGA | - | Thermogravimetric Analysis |
| TGA | - | Thermogravimetric Analyzer |
| UNFCCC | - | United Nations Framework Convention on Climate Change |

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Due to the growing industrialization and growth of the population, the energy demand is continually rising, and the potential for energy resources is not sustaining with the escalating consumption. Even after multiplying energy output, developed countries are still experiencing difficulties balancing the supply and demand for energy because of growth pressure. By 2050, the world's oil supplies are predicted to be exhausted. Energy sources including coal, oil, natural gas, and others are used to offset the majority of the energy demand. A hazard to the global climate is posed by rising greenhouse Gases (GHG) emissions, specifically $CO_2$. Over 20 million metric tons of $CO_2$ were anticipated to be emitted into the environment annually in 2000, according to one estimate (Bridgwater, 2003).

In the future, this trend is likely to result in extreme natural disasters, such as excessive rainfall and floods, droughts, and local imbalances. These toxic gases discharged into the environment lead to changes in atmospheric conditions and degradation of human health. The challenge is to explore about alternative energy sources, which biomass offers. In 2005, according to statistics from the "International Energy Agency" (IEA), biomass accounted for 10% of the world's demand for primary energy (Abdullahi et al., 2017).

Palm oil leftovers are used to produce a significant quantity of biomass in Malaysia, Indonesia, and Nigeria (Yaro et al., 2022). The pellets and briquettes produced from these biomasses make appropriate fuels. Vegetable oil has been identified as one of the most efficacious renewable sources in many studies on biomass fuels (Meher et al., 2013). In Southeast Asia, biomass waste from the palm oil sector is a valuable source of renewable energy. With the rapid growth of the palm oil sector in Indonesia, Malaysia, and Thailand, the availability of these biomass resources is on the rise. There is a general oversupply of by-products in the palm oil value chain, and there is a poor utilization rate for these by-products. The shell fragments left over after the nut has been taken out and crushed in the palm oil mill are known as palm kernel shells (PKS) (Obibuzor et al., 2012). Since PKS are fibrous materials, they may be moved straight from the production line to the intended application in bulk. Along with dust-like fractions and minute fibers, small and large shell fractions are mixed together. When compared to other biomass leftovers, the kernel shell moisture content is low; estimates from several sources range between 11% and 13% (Zafar, 2022).

The reason why palm kernel shells possess a slightly greater heating value than ordinary lignocellulosic biomass is owing to the presence of palm oil leftovers in them (Asadullah et al., 2013). Palm kernel shells are a superior biomass fuel to other industrial waste because they have a consistent size distribution, are simple to handle and crush, and have little biological activity because of their low moisture content (Jeguirim, & Khiari, 2023).

Being compact and having a high calorific content, PKS has become a popular biomass product. Palm kernel shell has gained popularity as a source of renewable energy due to its high calorific values (4000 Kcal/kg on average) and low ash and Sulphur contents, particularly in nations with less fossil energy storage like Korea, Japan, and Europe (Dey et al., 2021) . In addition to that, apart from its compact size, its optimal natural density (1.1 $g/cm^{-3}$), also makes the palm kernel shell more convenient to store, handle, and transport than other industrial fuel resources.

Additionally, burning palm kernel shell produces far fewer damaging pollutants and greenhouse gases in the environment due to the relatively low ash and sulfur concentrations. Conventionally, the press fiber and kernel shell produced by palm oil mills have been utilized as solid fuels for steam boilers (Saidur et al., 2011). The steam produced is utilized to power electricity-generating turbines. The energy requirements of a palm oil mill may be more than adequately satisfied by these two solid fuels alone. By utilizing cogeneration with mesocarp fibers and kernel shells, the majority of palm oil mills in the area are energy self-sufficient. In Malaysia, Indonesia, and Thailand, the demand for palm kernel shells has grown significantly, pushing up the price to a level comparable to coal (Silalertruksa et al., 2012). Due to the advantages associated with Clean Development Mechanism (CDM), cement firms are already replacing coal with palm kernel shells.

Several techniques, including mechanical (chopping, palletizing, and briquetting), thermochemical (pyrolysis, combustion, gasification, and torrefaction), and biochemical (anaerobic digestion and fermentation) conversion processes, can be used to convert biomass into biofuels or bioenergy (Umar et al., 2021). The type of biomass (solid, liquid, or mixed sample), the desired energy product, and the properties and characteristics of the biomass, its intended use, the conversion costs, as well as storage and transportation considerations, are just a few of the factors that must be taken into account when choosing the most advantageous biomass conversion process from these options (Palamanit et al., 2019). This is because numerous kinds and forms of biofuels or bioenergy are produced when biomass is converted using these procedures. Biomass may be converted into biofuels via pyrolysis, which is one of the thermochemical conversion processes that produces a byproduct such as biochar, and pyrolysis gas.

Pyrolysis of biomass is the thermal breakdown of biomass that takes place without oxygen (K N et al., 2022). It is the foundational chemical reaction that naturally takes place in the first two seconds and is the precursor to both the gasification and combustion processes. The flexible and appealing process of pyrolysis can successfully produce heat, electricity and chemicals from solid biomass that can utilize a variety of biomass as feedstock. The feedstock's moisture content, which should be approximately 10%, has a significant impact on the pyrolysis process (Scott et al., 1999). High quantities of water are created at higher moisture contents, while at lower levels, there is a chance that the process will only produce dust rather than oil. There are two types of pyrolysis processes called slow pyrolysis and fast pyrolysis. The major product of slow pyrolysis, which takes many hours to finish, is biochar (Brown et al., 2011).

On the contrary hand, fast pyrolysis produces 60% bio-oil and just needs a few seconds to finish. It also provides 20% syngas and 20% charcoal. Considering the above discussed advantages associated with PKS as a biofuel, the current study has considered analyzing the potential of PKS's use as a solid biofuel (Zafar, 2009).

## 1.2 Problem Statement

In spite of the above discussed aspects and applicability of pyrolysis processes, the pyrolysis process of biomass is still associated with various challenges because of quality and quantity of pyrolysis products, which are impacted by various factors, which include, biomass type and properties, operating parameters, type of reactor, and pyrolysis type, among other mentionable factors (Mettler et al., 2012). The biochar produced from the pyrolysis process has a high carbon to hydrogen ratio and an inclination to self-polymerize due to the existence of many unsaturated alkene and alkyne linkages, hydrocarbons produced by the pyrolysis of solid carbonaceous sources are typically of poor economic value. To enhance the economics of pyrolysis operations, low value hydrocarbons are commonly hydrogenated in a hydrogenation reactor.

The focus on the various aspects which impact the process of pyrolysis of biomass is still significantly limited. Furthermore, there is a lack evaluation or analysis of hydrogenation in enhancing the fuel quality of solid fuel and there is still large opportunity for analysis in this area.

Finally, the existing calorific value (CV) of palm kernel shells is reported to be under 20 MJ/kg which is low compared to commercially available coal (25 MJ/kg) (Sukiran et al., 2017). The underlying reason behind the comparatively low CV of PKS is a lower level of elemental carbon, higher oxygen and fixed carbon, which contribute to the lower CV of PKS (Indrawan, & Susanto, 2022). The enhancement of palm kernel shells into a high heat content solid fuel is necessary in order to analyse the PKS potential as biofuel and become alternative fuel to replace coal and other conventional fuels.

## 1.3 Objective of Study

i. To study the potential of palm kernel shell waste as a solid biofuel by using pyrolysis and catalytic hydrogenation process.

ii. To analyse the effect of hydrogenation temperature on C-H bonding for higher calorific value PKS-derived biofuel.

## 1.4 Scope of Study

i. The use of palm kernel shell waste in the production of a solid biofuel (biochar).

ii. The implementation of hydrogenation of pyrolysis process in the production of a solid biofuel (biochar) from of palm kernel shell waste.

iii. The analysis of carbonization of hydrogenation at temperature 400°C (between "300 and 600°C") in the absence of air.

iv. The analysis of biochar as solid biofuel extracted from palm kernel shell.

## 1.5 Significant of Study

In the last decades the energy demand has elevated significantly due to constantly increased demand because of continuously expanding industries and comparatively limited availability of fossil fuels. It has resulted in considering other alternative sources of energy and fuels as well as replacements for conventional fossil fuels. In the process of replacing conventional sources of energy, biomass is a significantly favorable and applicable alternative. Biochar, a carbon-rich material produced by burning biomass in an environment with low oxygen levels, is regarded by some experts as the secret to revitalizing revitalising soil.

Biochar, which is relatively light and porous, may act as a sponge and provide a home for a variety of beneficial soil microbes that are proven to improve the health of the soil and plants. Decreased bioavailability of environmental contaminants, increased agricultural productivity, decreased greenhouse gas emissions and global warming, sequestered atmospheric carbon into the soil, decreased soil nutrient leaching losses, and elevated agricultural productivity are all benefits of using biochar, which has since evolved into a value-added product that supports the bioeconomy (Oni et al., 2019).

Thus, it is with the help of the current study, with the help of which, the potential to the use of palm kernel shell waste as a solid biofuel, that is biochar from pyrolysis would be revealed. It is with the help of the current study and associated findings with the help of which the potential of using PKS waste as a solid biofuel (biochar from pyrolysis) with the help of Hydrogenation could be revealed. The findings would act as a contributing factor in opening new avenues in the aspect of biofuels add resists associated increasing demands. The findings from the current study would also act as a contributing factor in understanding the impact of temperature on attaining a higher calorific value.

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