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Bio-oil from Oil Palm Shell Pyrolysis as Renewable Energy: A Review

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ABSTRACT

Oil palm shell (OPS) is biomass with high carbon and hydrogen content, so it has the potential to produce renewable energy through the thermochemical method. Pyrolysis is a relatively inexpensive thermochemical method that continuously converts biomass into valuable gas, bio-oil, and char products. Bio-oil is used directly to fuel boilers and furnaces or to produce fuel oil. This article reviews the pyrolysis process of biomass from oil palm shells, discussing the operating parameters that influence the pyrolysis process and the method of upgrading bio-oil. This review shows a relationship between biomass composition (cellulose, hemicellulose, and lignin) and bio-oil yield. The water content in the raw material needs to be controlled at around 10%. The optimum particle size is closely related to the biomass's natural structure and reactor type. The higher the ash and fixed carbon content, the lower the bio-oil yield. The optimum temperature for pyrolysis is between 450-550 °C. A high heating rate will increase the decomposition of biomass into bio-oil. Particle size and reactor type strongly influence feed rate, residence time, and reaction time. A fluidized bed reactor gives the highest bio-oil yield. Using plastic in co-pyrolysis and catalyst increases the heating value and decreases the oxygenated content.

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1. Introduction

The reduced production of fossil energy, especially oil, and the global commitment to reducing greenhouse gas emissions, has prompted the government to continuously increase the role of renewable energy to maintain energy security and independence [1]. The Indonesian government is committed to climate change adaptation in the Paris Agreement by accelerating the energy transition from fossil fuels to renewable energy or energi baru terbarukan (EBT). The government targets the EBT mix of 23% by 2025, equivalent to 92.2 Million Tonnes of Oil Equivalent (MTOE), a quarter of which is planned from biofuels or bahan bakar nabati (BBN). The impact of the COVID-19 pandemic has caused the supply of EBT to decline with a nominal value of around 23.6 - 36.6 million Barrels of Oil Equivalent (BOE). EBT development needs serious attention related to the target of the EBT mix of 23% by 2025 [2]. Researchers have identified biomass as a sustainable, renewable, and environmentally friendly energy source [3].

Biomass is a term used for all organic materials from a plant produced through photosynthesis using sunlight [4]. Biomass is a carbon-neutral material with lower greenhouse gas (GHG) emissions due to its lower nitrogen and sulfur content than petroleum and coal [5]. Biomass is considered the largest renewable and sustainable source of carbon for the production of biofuels as a source of abundant and inexpensive energy. It accounts for 14% of world energy consumption [6].

Biomass can be converted into fuel through several processes, including combustion, digestion, gasification, pyrolysis, fermentation, and catalytic reactions [4]. Pyrolysis is a relatively inexpensive process that continuously converts biomass into valuable gas, liquid, and char [7].

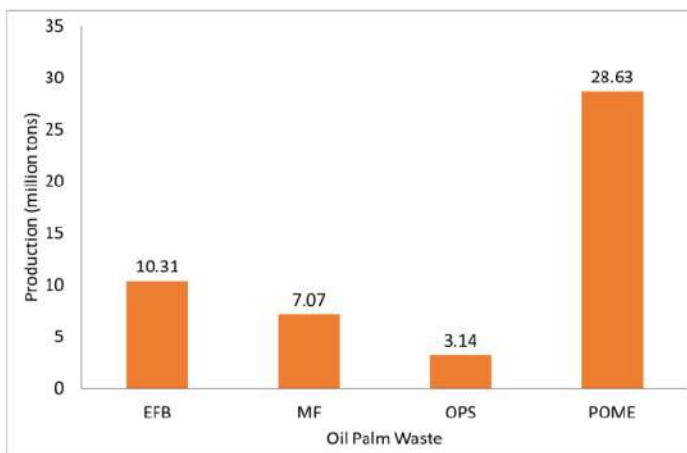


Fig. 1. Oil palm waste production in Indonesia in 2021 [8]

The production of EBT in biofuels relies heavily on crude palm oil (CPO) processing. The increase in crude palm oil (CPO) production in Indonesia has led to the rise of biomass waste from oil palm, including oil palm shells (OPS), empty fruit bunches (EFB), mesocarp fibers (MF), and palm oil mills effluent (POME) [9]. It is estimated that palm oil production in 2021 will be 49 million tons [10], with palm shell waste of 3.14 million tons (Fig. 1). This article contains a review of the pyrolysis process of biomass from oil palm shells, focusing on discussing the operating parameters that influence the pyrolysis process and the method of upgrading bio-oil.

2. Oil Palm Shell Biomass

Biomass is classified into four generations of biomass (Table 1). First-generation biomass refers to biomass from food crops such as sugarcane, starch, vegetable oils, and animal fats. The second generation is biomass from non-food and lignocellulosic plant residues such as wood, grass, and municipal solid waste. Meanwhile, the third generation biomass is the biomass from microalgae [11]. First-generation biomass as an energy source is limited because it competes with food demands [12].

Table 1. Biomass Classification by generation [11]

	1 st	2 nd	3 th	4 th
<i>Feedstock</i>	Sugarcane, grains, soybeans, corn, flours, vegetable oils, animal fats	Wood, agricultural waste, municipal solid waste, animal waste, grass, pulp sludge	Microalgae	Genetically modified crop
<i>Product</i>	Biodiesel, alcohol, corn ethanol	Hydrotreating oil, bio-oil, FT-oil	Algae oil	Biofuel
<i>Advantages</i>	Environmentally friendly, economical, and socially secure	We are not competing with food; environmentally friendly	High protein and residual nutrient algae can be used for jet fuel and animal feed.	Easily capture CO ₂ and convert it into carbon-neutral fuel.
<i>Disadvantages</i>	Limited, mixed with conventional fuel	Acidic, viscous, high oxygenated content	Slow growth, complicated and expensive algae extraction	-

3.1. Lignocellulose Pyrolysis Mechanism

The reaction mechanism of lignocellulose pyrolysis is based on the pyrolysis of three main components: cellulose, hemicellulose, and lignin. Several reactions occur during the pyrolysis process of lignocellulose, including dehydration, depolymerization, decarboxylation, isomerization, dehydrogenation, and fragmentation [29].

1) Cellulose Pyrolysis

Cellulose decomposition occurs at a temperature of 250-350 °C. Cellulose pyrolysis products are anhydrosugar (levoglucosan) as the main product, hydroxy acetaldehyde, acid, alcohol, char, and gas. Pyrolysis of cellulose produces a lot of CO gas due to the high carbonyl content and the carboxyl and carbonyl groups [29].

2) Hemicellulose Pyrolysis

Hemicellulose decomposition occurs at a temperature of 250-350 °C. The main product of hemicellulose pyrolysis is xylan; other products are furfural, ketone, phenol, acetic acid, and aldehyde. Hemicellulose pyrolysis produces much CO₂ gas due to the high carboxyl content [30].

3) Lignin Pyrolysis

Lignin decomposition occurs at a temperature of 300-550 °C [31]. The main products of lignin pyrolysis are phenol complexes (guaiacol, catechols, phenols) [32]. Chang et al. carried out the pyrolysis of various biomass. They stated that phenol is the main component in bio-oil from palm kernel shells produced from the decomposition of p-coumaryl alcohol in lignin [33]. Pyrolysis of lignin produces much H₂ gas due to the cracking of aromatic rings and CH₄ gas caused by methoxyl cracking [30].

3.2. Type of Pyrolysis

The distribution of solid, liquid, and gaseous products highly depends on the operating conditions during the pyrolysis process [27]. This indicates three types of pyrolysis: slow pyrolysis, fast pyrolysis, and flash pyrolysis [34]. All three differ in heating rate, temperature, residence time, and particle size [35].

1) Slow Pyrolysis

Slow pyrolysis is carried out at low temperature (< 500 °C), long residence time (can be hours or days), relatively large particle size (5-50 mm), and low heating rate (0.1-2 °C/seconds) with the main product in the form of biochar [29]. Lee et. al. [36] performed slow pyrolysis of oil palm shells at a heating rate of 18.9-20 °C/min, a temperature of 500-500.4 °C, and produced 27.5% biochar.

2) Fast Pyrolysis

This type is carried out with a high heating rate (10-20 °C/sec), relatively fast residence time (< 2 seconds) with a bio-oil yield of 50-70% [29]. Kim et. al. carried out pyrolysis at a temperature of 490 °C, the heating rate of 10-20 °C/min, and the residence time of about 0.5 seconds, and yielded 48.7% bio-oil [22]. Asadullah et. al. [13] conducted fast pyrolysis of oil palm shells at a temperature of 550 °C with a 56% bio-oil yield.

3) Flash Pyrolysis

This type of pyrolysis is carried out with a heating rate of 10³-10⁴ °C/sec, residence time <0.5 seconds, with a bio-oil yield of 75-80% [29]. Matamba et. al. [37] carried out flash pyrolysis of oil palm shells at a temperature of 600-900 °C and a pressure of 0.1-4.0 MPa, indicating that this process can be an effective method to increase the formation of H₂ gas and PAHs.

3.3. Process Parameter

Many factors affect the pyrolysis process, the product's amount, and the product's characteristics. These factors include the type and composition of biomass (lignocellulose, water content, ash, volatile, fixed carbon), pretreatment (physical, chemical, and biological), temperature, heating rate, residence time, atmospheric reaction, co-reactants, and reactor type [29, 34].

1) Biomass type and composition

Biomass with a high cellulose content will produce a lot of bio-oil because the decomposition of cellulose will have a higher volatile material which will be condensed during the pyrolysis

process [34]. However, Liu et. al. [38] studied the pyrolysis of a mixture of cellulose and lignin. They showed that the increase in bio-oil yield with increasing cellulose content was not proven, indicating that lignin inhibited cellulose pyrolysis to bio-oil. Wang et. al. [39] showed a weak interaction between cellulose, hemicellulose, and lignin.

2) Pretreatment

Biomass pretreatment includes thermal pretreatment (drying, torrefaction, hot water treatment), physics (crushing and grinding), chemical (acid/base treatment), biology (with fungi, enzymes, microbes), and a combination of the above methods [40, 41]. Various literature shows that before the pyrolysis process, oil palm shells undergo several treatments such as drying in the sun, refining, sifting, and drying in an oven for 24 hours at 105 °C. Then a proximate analysis was carried out to determine the volatile, fixed carbon, and water content using TGA. Ultimate analysis was conducted to determine the value of C, H, N, S, O, and ash/mineral content [42].

The high water content will inhibit temperature rise because some of the heat is used to evaporate water [27]. Based on the literature, the water content in the biomass feedstock is controlled at around 10% [43, 44]. Palm shells have a water content of about 10%. High water content in raw materials causes high water content in bio-oil products, reducing the calorific value of bio-oil [34] and phase separation in liquid yield [45, 46].

Biomass has a low thermal conductivity; therefore, reducing the biomass particle size can increase heat transfer efficiency to increase biomass decomposition [34]. The microscopic size will reduce the bio-oil produced because biomass decomposition occurs quickly. It gives enough time for the secondary reaction to happen to the pyrolysis vapor. As a result, it will increase the gas yield and reduce the liquid and char yield. The optimum particle size is closely related to the natural structure of the biomass and the reactor design [27].

The ash (mineral) content affects the yield of bio-oil. High ash content will reduce bio-oil yield and increase char and gas production. Abnisa et. al. [48] showed an increased biomass bio-oil output with lower ash content. The high content of NaCl and KCl will increase the formation of glycolaldehyde and decrease the formation of levoglucosan. While MgCl₂ and CaCl₂ will increase the formation of levoglucosan and furan [49]. The presence of sodium and potassium will reduce the yield of bio-oil. In contrast, the presence of sulfur and phosphorus with ammonium salt content significantly affects bio-oil yield and increases char formation [34].

Fixed carbon is carbon that is not evaporated during the heating process. The content of fixed carbon negatively correlates with the bio-oil yield; the higher fixed carbon content, the lower the bio-oil yield [34]. The high carbon content is suitable for manufacturing high-density briquettes [18].

Elemental analysis shows the biomass's chemical composition (C, H, N, S, O), and oxygen is obtained from the calculations. One of the characteristics of biomass is that it has low nitrogen and sulfur content compared to fossil fuels. The high aromatic and carbonation index is indicated by the high range of H and C compared to the oxygen content. A low O/C ratio characterizes the high heating value (HHV) because the chemical energy of the C-C bond is higher than that of the O-C bond [50].

3) Temperature

The efficiency of biomass conversion increases with increasing pyrolysis temperature until it reaches the peak temperature, producing maximum bio-oil [27]. The literature shows the optimum pyrolysis temperature is between 450-550 °C, but this value changes depending on the type of biomass and process variables [34]. Very high temperatures (above the optimum temperature) will reduce the amount of bio-oil produced due to a secondary reaction that converts volatile component (acid, alcohol, levoglucosan, furan) into non-condensable gas (CH₄, CO₂, CO) [51]. Abnisa et. al. [14] carried out the pyrolysis of oil palm shells in a fluidized bed reactor at temperatures between 400-800 °C and showed the highest bio-oil yields at a temperature of 500 °C.

4) Heating Rate

A high heating rate will increase the decomposition of biomass into bio-oil [34]. The process with a high heating rate and temperature will reduce mass and heat transfer limitations, thus producing more bio-oil [47]. For fast pyrolysis, increased heating and cooling rates can

Table 4. Type of Catalyst

Group	Catalyst	Ref.
Acid	Micropores (HZSM-5, Fluid catalytic cracking (FCC), ZSM-5) Macropores (MesoMFI, Al-SBA-15, Al-MSU-F)	[58][60][61][62]
Alkali	Alkali & alkali earth metal (CaO, MgO, ZnO, K ₂ CO ₃ , Ca(OH) ₂) Bentonite, Dolomite, Olivine	[62][63][64]
Neutral	Graphite nanofiber	[61]

The bio-oil quality can be evaluated from O/C, H/C, and HHV values. The low value of O/C and high value of H/V and HHV indicate the high quality of bio-oil [5, 65]. Likewise, bio-oil quality can be evaluated based on the functional groups in bio-oil and the content of oxygenated and aromatic compounds before and after the pyrolysis process. The lower the range of oxygenate compounds and the higher the content of aromatic compounds, the better the quality of the bio-oil [66]. Compared to commercial fuels (diesel and gasoline), oil palm shell bio-oil has a higher O/C content. The addition of plastic and catalyst can increase the calorific value but is still low compared to commercial fuels [66].

The problem with catalytic pyrolysis is coke's formation and the catalyst's deactivation [57]. The coke's formation can accelerate the catalyst's deactivation, close the catalyst pores, and poison the catalyst [67]. The formation of coke is caused by too small pore size as in the micropores of the catalyst (HZSM-5, ZSM-5), which inhibits the mass transfer of significant components [27]. This problem can be solved by using mesoporous catalysts with a high acidity level and a larger pore size (0.10-0.59 nm) [68]. The modification of the zeolite catalyst (HZSM-5/ZSM-5) through metal doping (such as Ga, Mo, Co, Ni, Zn, Fe, Z, Pd, and Pt) can increase aromatic production [69, 70]. Adding plastics with a high hydrogen content can increase conversion efficiency and reduce coke formation [57].

6. Knowledge Gap

This review discusses the operating parameters that influence the pyrolysis process and the methods of upgrading bio-oil. However, bio-oil quality does not meet the quality standards of commercial fuels. So it is necessary to study an upgrading process that can produce high-quality fuel or valuable chemical products such as hydrotreatment to reduce oxygen content, supercritical water method to increase heating value, supercritical fluids, and esterification of bio-oils. Likewise, economic feasibility studies, resource conservation systems, and heat integration techniques on the pyrolysis process of oil palm shells are still limited; this indicates the potential for future research.

7. Conclusion

This review discusses the operating parameters that influence the pyrolysis process and the methods of upgrading bio-oil in the pyrolysis process, namely co-pyrolysis and catalytic cracking. The result shows a relationship between biomass composition (cellulose, hemicellulose, and lignin) and bio-oil yield. The water content in the raw material needs to be controlled at around 10%. The optimum particle size is closely related to the biomass's natural structure and reactor type. The higher the ash and the fixed carbon content, the lower the bio-oil yield. The optimum temperature for pyrolysis is between 450-550 °C. A high heating rate will increase the decomposition of biomass into bio-oil. Particle size and reactor type strongly influence feed rate, residence time, and reaction time. The fluidized bed reactor type gives the highest average bio-oil yield of 59.16 wt.%. The use of plastics in co-pyrolysis and catalyst increases the heating value and decreases the oxygen content. The use of polystyrene (PS) in oil palm shells co-pyrolysis increases the heating value from 6.58 to 40.34 MJ/kg and decreases the oxygen content from 71.40 to 10.50 wt.%. Using a catalyst (ZSM-5) increases the heating value from 6.58 to 28.9 MJ/kg and decreases the oxygen content from 71.40 to 19.92 wt.%.

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