

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 dan 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].

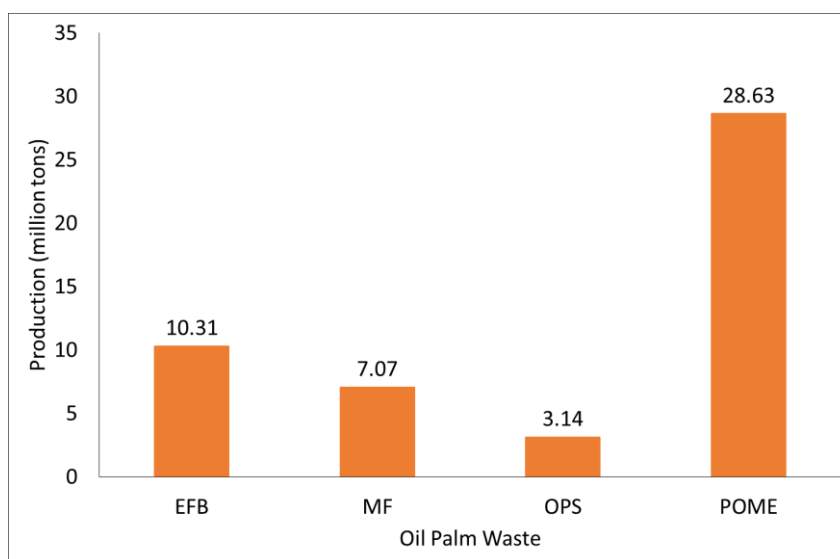


Fig. 1. Oil palm waste production in Indonesia in 2021 [8]

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 | - |

Oil palm shell is second-generation biomass rich in carbon and hydrogen and similar to hardwood [13], thus making palm shells a superior raw material for producing biofuels, valuable chemical products, or energy through thermochemical methods [14]. The oil palm shell is one of the lignocellulosic biomass, containing three main components: cellulose, hemicellulose, and lignin [15]. Cellulose is the essential component in biomass because it has the most significant percentage and contains a long linear chain of β -(1,4)-glycoside composed of D-glucose monomers [16]. Hemicellulose is a polysaccharide complex in the cell wall and cellulose, which acts as a connecting element between cellulose and lignin [17]. Lignin is a non-carbohydrate component of wood with a polyphenol structure that plays a role in building cell walls and combining all cells into one [15].

Oil palm shells contain about 24% hemicellulose, 50% lignin, and 30% cellulose. Compared to fossil fuels, oil palm shells have lower nitrogen content ($<1\%$), lower sulfur content ($<0.2\%$), and higher oxygen content (40-50%). The low nitrogen and sulfur content will reduce the content of NO_x and SO_x , a greenhouse gas. The high carbon content is suitable for manufacturing high-density briquettes [18]. The proximate and ultimate analysis of oil palm shells is shown in table 2.

Table 2. Palm shell proximate dan ultimate analysis

| Proximate Analysis | Value (wt%) | | | | | Ultimate Analysis | Value (wt%) | | | | |
|--------------------|-------------|-------|-------|------|------|-------------------|-------------|-------|-------|-------|------|
| Moisture Content | 5.69 | 7.96 | 12.69 | 9.4 | 11 | Carbon | 46.92 | 50.01 | 51.56 | 44.56 | 50.7 |
| Volatile | 69.10 | 72.47 | 75.14 | 82.5 | 67.2 | Hydrogen | 8.95 | 6.85 | 6.31 | 5.22 | 6.0 |
| Fixed Carbon | 23.49 | 18.7 | 22.05 | 1.4 | 19.7 | Nitrogen | 1.15 | 1.90 | 0.7 | 0.4 | 0.4 |
| Ash | 1.72 | 1.1 | 2.81 | 6.7 | 2.1 | Sulfur | 2.35 | - | 0.1 | 0.05 | 0.1 |
| | | | | | | Oxygen | 40.63 | 41.15 | 41.33 | 49.77 | 42.8 |
| Ref. | [19] | [20] | [21] | [22] | [23] | | [19] | [20] | [21] | [22] | [24] |

Biochemical and thermochemical can convert biomass into solid, liquid, and gaseous fuels, including extraction, hydrolysis, and fermentation [25]. It takes a long time and has a low yield. Thermochemical conversion includes combustion, gasification, and pyrolysis process that produces heat. Gasification is the thermochemical conversion of raw materials into syngas through chemical reactions at high temperatures under controlled oxygen conditions [26].

3. Oil Palm Shell Biomass Pyrolysis

Thermochemical conversion has advantages over other technologies, one of which is pyrolysis. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen. This process is more promising because it is more flexible in selecting raw materials (no need to pay attention to the type, shape, and physical and chemical properties). It can be operated over a wide temperature range and at atmospheric pressure, producing three products (solid, liquid, and gas) [27]. Pyrolysis is a complex reaction [28]; pyrolysis is carried out for three primary purposes: (1) to produce smokeless fuel (clean in combustion), (2) to have energy with a higher heating value than the raw material, and (3) to make more reactive power [4]. The schematic of biomass pyrolysis is shown in Fig. 2.

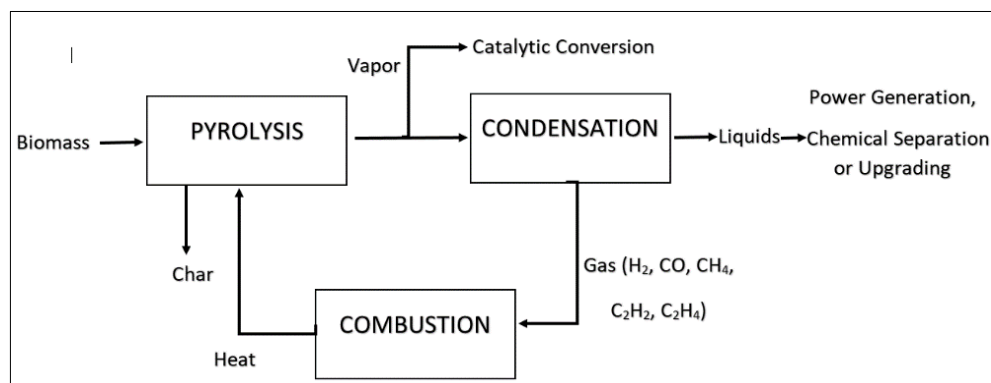


Fig. 2. Pyrolysis process schematic

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, phenol) [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 the 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 components (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

minimize secondary reactions. The high heating rate will inhibit the dehydration reaction, reducing the bio-oil water content [34]. The oxygen content also decreases with the increasing heating rate; this proves that the formation of oxygen-containing gases such as CO₂ or CO increases with increasing heating rate [47].

5) *Feed Rate*

Feed rate is an important parameter in the continuous pyrolysis process [34]. According to Wu et. al. [53], increasing the feed rate will increase the production of condensed vapor, reduce the residence time of vapor in the reactor, and prevent secondary cracking reactions, thereby increasing bio-oil yield. Kim et. al. [22] carried out the pyrolysis of palm shells in a fluidized bed at a temperature of 490 °C with a feed rate of 10 g/min and 5 g/min and showed that at a feed rate of 10 g/min produced the most bio-oil by 50%. Asadullah et. al. [13], in a fluidized bed at a temperature of 550 °C with a feed rate of 3-10 g/min showed the highest bio-oil yield at a feed rate of 10 g/min.

6) *Vapor Residence Time (Inert Gas Flow rate)*

Pyrolysis vapor can undergo secondary reactions from thermal cracking, depolymerization, and recondensation, which causes a decrease in bio-oil yield [29]. Therefore, taking vapor quickly from the reaction zone is necessary to minimize secondary reactions. The higher the gas flow rate, the shorter the residence time of the moisture in the pyrolysis reaction zone. Gas flow velocity that is too high can reduce bio-oil yield due to incomplete condensation of vapor and carry some of the biomass out of the reactor before the pyrolysis process is completed [53]. Qureshi et. al. carried out the pyrolysis of oil palm shells in a fixed bed reactor at a temperature of 500 °C with a residence time of 0.25-15 seconds. The highest yield was at 0.25 seconds [40].

7) *Reaction Time*

Reaction time is when the biomass is maintained at a specific pyrolysis temperature. An extended reaction time can cause secondary reactions to pyrolysis vapor, such as carbonization, gasification, and thermal cracking, which decrease bio-oil yield [54]. Qureshi et. al. in a fixed bed reactor at a temperature of 500 °C with a reaction time of 20-60 minutes, the highest yield was at 30 minutes [40]. Abnisa et. al. [14] in a fluidized bed at a temperature of 500 °C with a reaction time of 30-150 minutes, the highest yield was at 60 minutes.

8) *Reactor Type*

Several types of reactors have been investigated to obtain high bio-oil yields. Drum, rotary, and screw feed reactors are usually used for slow pyrolysis. Fast pyrolysis uses a microwave, tandem micro, fixed bed, ablative, and fluidized bed. Other reactors used in the pyrolysis process include circulating fluidized bed, rotating cone, vacuum, and solar reactor. Several types of reactors are widely used in the oil palm shell pyrolysis process based on the literature, for example, fluidized bed reactor [14], fixed-bed reactor [19], tandem micro-reactor [55], and microwave [56]. Fig. 3 shows that the fluidized bed reactor gives an average bio-oil yield of 59.16 wt.%, while the fixed bed reactor gives an average bio-oil yield of 44.00 wt.%.

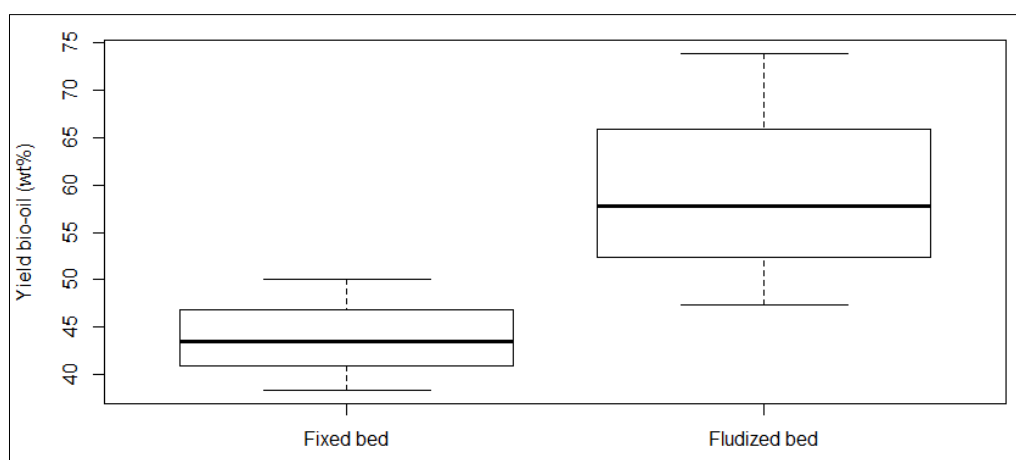


Fig. 3. Bio-oil yield in the most widely used reactor for oil palm pyrolysis

4. Bio-oil

Bio-oil is a liquid product of the pyrolysis process and has several applications. Bio-oil is used directly to fuel boilers and furnaces or to produce fuel oil and chemical products [44]. Bio-oil produced from palm shells has high oxygen content (56-72 wt%), high moisture content (25-53), low pH (2.5-3.5), and low calorific value (6-19 MJ/kg), which are not commercially attractive (Table 3). The high oxygen content is due to the presence of oxygenated compounds. Oil palm shells have a high lignin content, which results in phenol complexes (oxygenate compounds) as the most significant component in the bio-oil produced. The calorific value of oil palm shells is the highest compared to other palm oil wastes due to the high lignin content. However, a high lignin content will produce biochar, thereby reducing bio-oil yield [27]. Therefore, it is necessary to continue upgrading by co-pyrolysis or adding a catalyst or a combination of both [24]. Table 3 shows the characteristic of upgraded bio-oil palm shell/polystyrene co-pyrolysis and catalytic pyrolysis using alumina, zeolite socony mobile-5 (ZSM-5), equilibrium catalyst (E-cat), activated carbon (AC), lignite char (LC), and NiMoS/ γ -Al₂O₃.

Table 3. Characteristics of pyrolysis bio-oil and the effect of the upgrading process

| Characteristic | OPS | OPS/PS | Alumina | ZSM-5 | E-cat | AC | LC | NiMoS/ γ -Al ₂ O ₃ |
|----------------------------|-------|--------|---------|-------|-------|-------|-------|--|
| Temperature, °C | 500 | 600 | 485 | 485 | 485 | 500 | 500 | 550 |
| Calorific Value, MJ/kg | 6.58 | 40.34 | 23.2 | 28.9 | 31.3 | 18.79 | 31.13 | 29.3 |
| Moisture Content, % | 53 | 1.9 | 32.1 | 42.9 | 33.5 | - | - | - |
| Viscosity, cP | 3.2 | 8.28 | | | | | | |
| pH | 2.5 | 2.8 | - | - | - | - | - | - |
| Density, kg/m ³ | 1051 | 1058 | 1200 | 1200 | 1170 | | | |
| Carbon, wt% | 19.48 | 81.34 | 51.59 | 64.42 | 69.2 | 50.94 | 66.68 | - |
| Hydrogen, wt% | 8.92 | 7.79 | 6.98 | 7.28 | 9.04 | 4.72 | 6.41 | - |
| Oxygen, wt% | 71.40 | 10.50 | 34.60 | 19.92 | 14.5 | 43.91 | 25.78 | - |
| Nitrogen, wt% | 0.2 | - | 6.65 | 7.93 | 6.79 | 0.68 | 1.02 | - |
| Sulfur, wt% | 0.04 | - | 0.18 | 0.45 | 0.47 | - | - | - |
| O/C | | 0.1 | 0.5 | 0.23 | 0.16 | 0.65 | 0.3 | 0.12 |
| H/C | | 1.5 | 1.62 | 1.36 | 1.57 | 1.11 | 1.12 | - |
| TAN, mgKOH/g | 207 | | 207 | 201 | 171 | - | - | 51.9 |
| Ref. | [14] | [57] | [58] | [58] | [58] | [56] | [56] | [59] |

5. Upgrading

The pyrolysis process upgrades include reducing the oxygenate content in bio-oil through deoxygenation reactions. It includes dehydration, decarboxylation, and decarbonylation by adding a catalyst or plastic in the pyrolysis process (Table 3). Plastic is added in co-pyrolysis because it has a high carbon and hydrogen content (H/C value close to 2), thus providing a sufficient hydrocarbon pool to react with the oxygen in the bio-oil [14]. Polypropylene (PP), Low-Density Polyethylene (LDPE), and High-Density Polyethylene (HDPE) plastics are suitable for use in co-pyrolysis with biomass from palm oil because they have a high hydrogen content (about 14%) [27]. Using plastic in co-pyrolysis will improve the bio-oil quality by increasing carbon content, heating value, and decreasing oxygen content [27]. Abnisa et. al. [57] showed an increase in carbon content from 19.48 to 81.34 wt%, an increase in calorific value from 6.58 to 40.34 MJ/kg, and a decrease in oxygen from 71.40 to 10.50 wt%, while hydrogen is constant.

Deoxygenation can also be done with a catalyst to increase the selectivity of the desired component in the resulting bio-oil. Catalysts are grouped into acidic, basic, and neutral catalysts (Table 4). Acid catalysts such as HZSM-5/ZSM-5 with high acidity show superior performance for aromatization. Lewis and Bronsted acid sites in HZSM-5 promote cracking and cleavage of C-O and C-C bonds in oxygenating components. Through acid catalysis, deoxygenation, oligomerization, dehydrogenation, and dealkylation [27].

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 (0.52-0.59 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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References

- [1] Tim Sekretaris Jenderal Dewan Energi Nasional, "Indonesia Energy Outlook 2019," *J. Chem. Inf. Model.*, vol. 53, no. 9, pp. 1689–1699, 2019.
- [2] E. Hilmawan and A. Sugiyono, *OUTLOOK ENERGI INDONESIA 2020 Dampak Pandemi COVID-19 terhadap Sektor Energi di Indonesia*, no. August. 2020.
- [3] I. M. Rajendra, I. N. S. Winaya, A. Ghurri, and I. K. G. Wirawan, "Pyrolysis study of coconut leaf's biomass using thermogravimetric analysis," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 539, no. 1, 2019, DOI: 10.1088/1757-899X/539/1/012017.
- [4] A. Singh, K. S. Rawat, O. P. Nautiyal, and T. V. Chavdal, "Biomass To Fuel: Conversion Techniques," *Energy Resour. Dev. Harvest. Manag.*, no. September, pp. 155–194, 2016.
- [5] X. Hu and M. Gholizadeh, "Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialization stage," *J. Energy Chem.*, vol. 39, no. x, pp. 109–143, 2019, DOI: 10.1016/j.jechem.2019.01.024.
- [6] L. Dai *et al.*, "Integrated process of lignocellulosic biomass torrefaction and pyrolysis for upgrading bio-oil production: A state-of-the-art review," *Renew. Sustain. Energy Rev.*, vol. 107, no. February, pp. 20–36, 2019, DOI: 10.1016/j.rser.2019.02.015.
- [7] R. K. Ahmad, S. A. Sulaiman, M. Inayat, and H. A. Umar, "Effects of Process Conditions on Calorific Value and Yield of Charcoal Produced from Pyrolysis of Coconut Shells Effects of Process Conditions on Calorific Value and Yield of Charcoal Produced from Pyrolysis of Coconut Shells," no. September 2020, DOI: 10.1007/978-981-15-5753-8.
- [8] Badan Pengelola Dana Perkebunan Sawit, "Potensi Limbah Kelapa Sawit Indonesia," www.bpdp.or.id. <https://www.bpdp.or.id/Potensi-Limbah-Kelapa-Sawit-Indonesia> (accessed Aug. 9, 2022).
- [9] A. Haryanti, Norsamsi, P. S. F. Sholiha, N. P. Putri, "Studi Pemanfaatan Limbah Padat Kelapa Sawit," *Konversi*, vol. 3, no. 2, 2014.
- [10] Direktorat Jenderal Perkebunan, "Produksi Kelapa Sawit Menurut Provinsi di Indonesia, 2017-2021 Palm Oil Production by Province in Indonesia, 2017-2021," vol. 2021, p. 2021, 2021.
- [11] H. Chowdhury and B. Loganathan, "Third-generation biofuels from microalgae: a review," *Curr. Opin. Green Sustain. Chem.*, vol. 20, pp. 39–44, 2019, DOI: 10.1016/j.cogsc.2019.09.003.
- [12] R. Alayoubi *et al.*, "Low-temperature ionic liquid pretreatment of lignocellulosic biomass to enhance bioethanol yield," *Renew. Energy*, vol. 145, pp. 1808–1816, 2020, DOI: 10.1016/j.renene.2019.07.091.
- [13] M. Asadullah, N. Suhada, A. Rasid, S. Aishah, S. A. Kadir, and A. Azdarpour, "Production and detailed characterization of bio-oil from fast pyrolysis of palm kernel shell," *Biomass and Bioenergy*, vol. 59, pp. 316–324, 2013, DOI: 10.1016/j.biombioe.2013.08.037.
- [14] F. Abnisa, W. M. A. W. Daud, W. N. W. Husin, and J. N. Sahu, "Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in the pyrolysis process," *Biomass and Bioenergy*, vol. 35, no. 5, pp. 1863–1872, 2011, DOI: 10.1016/j.biombioe.2011.01.033.
- [15] P. A. Meyer, L. J. Snowden-Swan, S. B. Jones, K. G. Rappé, and D. S. Hartley, "The effect of feedstock composition on fast pyrolysis and upgrading to transportation fuels: Techno-economic analysis and greenhouse gas life cycle analysis," *Fuel*, vol. 259, no. March 2019, p. 116218, 2020, DOI: 10.1016/j.fuel.2019.116218.
- [16] T. A. Khan, A. S. Saud, S. S. Jamari, M. H. A. Rahim, J. W. Park, and H. J. Kim, "Hydrothermal carbonization of lignocellulosic biomass for carbon-rich material preparation: A review," *Biomass and Bioenergy*, vol. 130, no. October 2018, p. 105384, 2019, DOI: 10.1016/j.biombioe.2019.105384.
- [17] F. X. Collard and J. Blin, "A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses, and lignin," *Renew. Sustain. Energy Rev.*, vol. 38, pp. 594–608, 2014, DOI: 10.1016/j.rser.2014.06.013.
- [18] G. Chang, P. Shi, Y. Guo, L. Wang, and C. Wang, "Enhanced pyrolysis of palm kernel shell wastes to bio-based chemicals and syngas using red mud as an additive," *J. Clean. Prod.*, vol. 272, p. 122847, 2020, DOI: 10.1016/j.jclepro.2020.122847.

- [19] J. O. Ogunkanmi, D. M. Kulla, N. O. Omisanya, M. Sumaila, and D. O. Obada, "Case Studies in Thermal Engineering Extraction of bio-oil during pyrolysis of locally sourced palm kernel shells : Effect of process parameters," *Case Stud. Therm. Eng.*, vol. 12, no. September, pp. 711–716, 2018, doi: 10.1016/j.csite.2018.09.003.
- [20] W. M. A. W. Daud and W. S. W. Ali, "Comparison on pore development of activated carbon produced from palm shell and coconut shell," *Bioresour. Technol.*, vol. 93, no. 1, pp. 63–69, 2004, doi: 10.1016/j.biortech.2003.09.015.
- [21] Z. Ma, D. Chen, J. Gu, B. Bao, and Q. Zhang, "Determination of pyrolysis characteristics and kinetics of palm kernel shell using TGA-FTIR and model-free integral methods," *Energy Convers. Manag.*, vol. 89, pp. 251–259, 2015, doi: 10.1016/j.enconman.2014.09.074.
- [22] S. Kim, S. Jung, and J. Kim, "Bioresource Technology Fast pyrolysis of palm kernel shells : Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds," *Bioresour. Technol.*, vol. 101, no. 23, pp. 9294–9300, 2010, doi: 10.1016/j.biortech.2010.06.110.
- [23] F. Abnisa, W. M. A. W. Daud, W. N. W. Husin, and J. N. Sahu, "Utilization possibilities of palm shell as a source of biomass energy in Malaysia by producing bio-oil in the pyrolysis process," *Biomass and Bioenergy*, vol. 35, no. 5, pp. 1863–1872, 2011, doi: 10.1016/j.biombioe.2011.01.033.
- [24] G. Chang, P. Miao, H. Wang, L. Wang, X. Hu, and Q. Guo, "A synergistic effect during the co-pyrolysis of Nannochloropsis sp. and palm kernel shell for aromatic hydrocarbon production," *Energy Convers. Manag.*, vol. 173, no. August, pp. 545–554, 2018, doi: 10.1016/j.enconman.2018.08.003.
- [25] S. N. Naik, V. V. Goud, P. K. Rout, and A. K. Dalai, "Production of first and second generation biofuels: A comprehensive review," *Renew. Sustain. Energy Rev.*, vol. 14, no. 2, pp. 578–597, 2010, doi: 10.1016/j.rser.2009.10.003.
- [26] T. Damartzis and A. Zabaniotou, "Thermochemical conversion of biomass to second generation biofuels through integrated process design — A review," vol. 15, pp. 366–378, 2011, doi: 10.1016/j.rser.2010.08.003.
- [27] L. Melia *et al.*, "Bio-oil production from pyrolysis of oil palm biomass and the upgrading technologies : A review," *Carbon Resour. Convers.*, vol. 4, no. June, pp. 239–250, 2021, doi: 10.1016/j.crcon.2021.10.002.
- [28] N. Aini, S. Jamilatun, J. Pitoyo, " Effect of Biomass Types on Products of Pyrolysis: A Review," *Agroindustrial Technology Journal* Vol.06 No.01 (2022) 89-101 DOI: <http://dx.doi.org/10.21111/atj.v6i1.7559>.
- [29] T. Kan, V. Strezov, and T. J. Evans, "Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters," *Renew. Sustain. Energy Rev.*, vol. 57, pp. 1126–1140, 2016, doi: 10.1016/j.rser.2015.12.185.
- [30] H. Yang, R. Yan, H. Chen, D. H. Lee, and C. Zheng, "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *fuel*, vol. 86, no. 12–13, pp. 1781–1788, 2007, doi: 10.1016/j.fuel.2006.12.013.
- [31] Y. K N *et al.*, "Lignocellulosic biomass-based pyrolysis: A comprehensive review," *Chemosphere*, vol. 286, no. P2, p. 131824, 2022, doi: 10.1016/j.chemosphere.2021.131824.
- [32] S. D. Stefanidis, K. G. Kalogiannis, E. F. Iliopoulou, C. M. Michailof, P. A. Pilavachi, and A. A. Lappas, "Journal of Analytical and Applied Pyrolysis A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose, and lignin," *J. Anal. Appl. Pyrolysis*, vol. 105, pp. 143–150, 2014, doi: 10.1016/j.jaap.2013.10.013.
- [33] G. Chang *et al.*, "The lignin pyrolysis composition and pyrolysis products of palm kernel shell, wheat straw, and pine sawdust," *Energy Convers. Manag.*, vol. 124, pp. 587–597, 2016, doi: 10.1016/j.enconman.2016.07.038.
- [34] R. E. Guedes, A. S. Luna, and A. R. Torres, "Journal of Analytical and Applied Pyrolysis Operating parameters for bio-oil production in biomass pyrolysis : A review," *J. Anal. Appl. Pyrolysis*, vol. 129, no. July 2017, pp. 134–149, 2018, doi: 10.1016/j.jaap.2017.11.019.

- [35] O. Azeta, A. O. Ayeni, O. Agboola, and F. B. Elehinafe, "A review on the sustainable energy generation from the pyrolysis of coconut biomass," *Sci. African*, vol. 13, p. e00909, 2021, doi: 10.1016/j.sciaf.2021.e00909.
- [36] X. J. Lee, L. Y. Lee, B. Y. Z. Hiew, S. Gan, S. Thangalazhy-Gopakumar, and H. K. Ng, "Valorisation of oil palm wastes into high yield and energy content biochars via slow pyrolysis: Multivariate process optimization and combustion kinetic studies," *Mater. Sci. Energy Technol.*, vol. 3, pp. 601–610, 2020, doi: 10.1016/j.mset.2020.06.006.
- [37] T. Matamba, A. Tahmasebi, S. Khoshk Rish, and J. Yu, "Promotion Effects of Pressure on Polycyclic Aromatic Hydrocarbons and H₂ Formation during Flash Pyrolysis of Palm Kernel Shell," *Energy & Fuels*, vol. 34, no. 3, pp. 3346–3356, Mar. 2020, doi: 10.1021/acs.energyfuels.9b04409.
- [38] Z. Liu, Y. Zhang, and Z. Li, "Cellulose-lignin and Xylan-lignin Interactions on the Formation of Lignin-derived Phenols in Pyrolysis Oil," no. March 2018, 2017, doi: 10.15376/biores.12.3.4958-4971.
- [39] S. Wang, X. Guo, K. Wang, and Z. Luo, "Journal of Analytical and Applied Pyrolysis Influence of the interaction of components on the pyrolysis behavior of biomass," *J. Anal. Appl. Pyrolysis*, vol. 91, no. 1, pp. 183–189, 2011, doi: 10.1016/j.jaap.2011.02.006.
- [40] K. M. Qureshi *et al.*, "Journal of Analytical and Applied Pyrolysis A technical review on semi-continuous and continuous pyrolysis process of biomass to bio-oil," *J. Anal. Appl. Pyrolysis*, vol. 131, no. December 2017, pp. 52–75, 2018, doi: 10.1016/j.jaap.2018.02.010.
- [41] Y. Zheng, J. Zhao, F. Xu, and Y. Li, "Pretreatment of lignocellulosic biomass for enhanced biogas production," *Prog. Energy Combust. Sci.*, vol. 42, pp. 35–53, 2014, doi: 10.1016/j.pecs.2014.01.001.
- [42] K. K. Zaman, V. Balasundram, N. Ibrahim, and M. D. Muhaimin, "Effect of Particle Size and Temperature on Pyrolysis of Palm Kernel Shell Effect of Particle Size and Temperature on Pyrolysis of Palm Kernel Shell," no. November, 2018, doi: 10.14419/ijet.v7i4.35.22339.
- [43] M. Danish, M. Naqvi, U. Farooq, and S. Naqvi, "Characterization of South Asian Agricultural Residues for Potential Utilization in Future 'energy mix ' Characterization of South Asian agricultural residues for potential utilization in future 'energy mix,'" *Energy Procedia*, vol. 75, no. August, pp. 2974–2980, 2015, doi: 10.1016/j.egypro.2015.07.604.
- [44] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68–94, 2012, doi: 10.1016/j.biombioe.2011.01.048.
- [45] K. Onarheim, Y. Solantausta, and J. Lehto, "Process Simulation Development of Fast Pyrolysis of Wood Using Aspen Plus," *Energy & Fuels*, vol. 29, no. 1, pp. 205–217, Jan. 2015, doi: 10.1021/ef502023y.
- [46] Q. Cheng, M. Jiang, Z. Chen, X. Wang, and B. Xiao, "Pyrolysis and kinetic behavior of banana stem using thermogravimetric analysis," *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 38, no. 22, pp. 3383–3390, Nov. 2016, doi:10.1080/15567036.2016.1153754.
- [47] J. Akhtar, N. Saidina, and P. Wood, "A review on operating parameters for optimum liquid oil yield in biomass pyrolysis," *Renew. Sustain. Energy Rev.*, vol. 16, no. 7, pp. 5101–5109, 2012, doi: 10.1016/j.rser.2012.05.033.
- [48] F. Abnisa, A. Arami-niya, W. M. A. W. Daud, J. N. Sahu, and I. M. Noor, "Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis," *Energy Convers. Manag.*, vol. 76, pp. 1073–1082, 2013, doi: 10.1016/j.enconman.2013.08.038.
- [49] R. C. Brown, R. O. Fox, and J. A. Koziel, "Understanding the product distribution from biomass fast pyrolysis," 2010.
- [50] C. E. M. Braza and P. M. Crnkovic, "Physical-Chemical Characterization of Biomass Samples for Application in Pyrolysis Process," *Chem. Eng. Trans.*, vol. 37, pp. 523–528, Jan. 2014, doi: 10.3303/CET1437088.
- [51] C. K. Ling, H. P. San, E. H. Kyin, L. S. Hua, L. W. Chen, and C. Y. Yee, "Yield and calorific value of bio-oil pyrolyzed from oil palm biomass and its relation with solid residence time and process temperature," *Asian J. Sci. Res.*, vol. 8, no. 3, pp. 351–358, 2015, doi: 10.3923/ajsr.2015.351.358.

- [52] S. Wu, C. Chang, Y. Chang, and H. Wan, "Comparison of oil-tea shell and Douglas-fir sawdust for the production of bio-oils and chars in a fluidized-bed fast pyrolysis system," *FUEL*, vol. 175, pp. 57–63, 2016, doi: 10.1016/j.fuel.2016.02.008.
- [53] C. H. Biradar, K. A. Subramanian, and M. G. Dastidar, "Production and fuel quality upgradation of pyrolytic bio-oil from *Jatropha Curcas* de-oiled seed cake," *fuel*, vol. 119, pp. 81–89, 2014, doi: 10.1016/j.fuel.2013.11.035.
- [54] M. Bartoli, L. Rosi, A. Giovannelli, P. Frediani, and M. Frediani, "Production of bio-oils and bio-char from *Arundo donax* through microwave-assisted pyrolysis in a multimode batch reactor," *J. Anal. Appl. Pyrolysis*, vol. 122, pp. 479–489, 2016, doi: 10.1016/j.jaap.2016.10.016.
- [55] P. Ghorbannezhad, F. Kool, H. Rudi, and S. Ceylan, "Sustainable production of value-added products from fast pyrolysis of palm shell residue in tandem micro-reactor and pilot plant," *Renew. Energy*, vol. 145, pp. 663–670, 2020, doi: 10.1016/j.renene.2019.06.063.
- [56] J. E. Omoriyekomwan, A. Tahmasebi, and J. Yu, "Production of phenol-rich bio-oil during catalytic fixed-bed and microwave pyrolysis of palm kernel shell," *Bioresour. Technol.*, vol. 207, pp. 188–196, May 2016, doi: 10.1016/j.biortech.2016.02.002.
- [57] F. Abnisa and W. M. A. Wan Daud, "A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil," *Energy Convers. Manag.*, vol. 87, pp. 71–85, 2014, doi: 10.1016/j.enconman.2014.07.007.
- [58] S. Won, B. Seok, and D. Hyun, "Bioresource Technology Catalytic pyrolysis of palm kernel shell waste in a fluidized bed," *Bioresour. Technol.*, vol. 167, pp. 425–432, 2014, doi: 10.1016/j.biortech.2014.06.050.
- [59] V. Han-u-domlarypyos, P. Kuchonthara, P. Reubroycharoen, and N. Hinchiranan, "Quality improvement of oil palm shell-derived pyrolysis oil via catalytic," *fuel*, vol. 143, pp. 512–518, 2015, doi: 10.1016/j.fuel.2014.11.068.
- [60] Q. Niu *et al.*, "Journal of Analytical and Applied Pyrolysis Exploring catalytic pyrolysis of Palm Shell over HZSM-5 by gas Chromatography-mass spectrometry and photoionization mass spectrometry," *J. Anal. Appl. Pyrolysis*, vol. 152, no. October, p. 104946, 2020, doi: 10.1016/j.jaap.2020.104946.
- [61] C. K. Wai, S. Yusup, N. S. Muda, N. Zaheera, and A. Kapor, "Comparative Study of H-ZSM 5 Zeolite and Graphite Nanofiber (GNF) in Catalytic Pyrolysis of Oil Palm Fronds (OPF)," vol. 5, no. 3, pp. 14–20, 2016.
- [62] D. Ro *et al.*, "Bench scale catalytic fast pyrolysis of empty fruit bunches over low-cost catalysts and HZSM-5 using a fixed bed reactor," *J. Clean. Prod.*, vol. 176, pp. 298–303, 2018, doi: 10.1016/j.jclepro.2017.12.075.
- [63] Y. Yee, S. Thangalazhy-gopakumar, H. Kiat, L. Yee, and S. Gan, "Effect of oxide catalysts on the properties of bio-oil from in-situ catalytic pyrolysis of palm empty fruit bunch fiber," *J. Environ. Manage.*, vol. 247, no. June, pp. 38–45, 2019, doi: 10.1016/j.jenvman.2019.06.049.
- [64] M. Auta, L. M. Ern, and B. H. Hameed, "Journal of Analytical and Applied Pyrolysis Fixed-bed catalytic and non-catalytic empty fruit bunch biomass pyrolysis," *J. Anal. Appl. Pyrolysis*, vol. 107, pp. 67–72, 2014, doi: 10.1016/j.jaap.2014.02.004.
- [65] T. Dickerson and J. Soria, "Catalytic fast pyrolysis: A review," *Energies*, vol. 6, no. 1, pp. 514–538, 2013, doi: 10.3390/en6010514.
- [66] S. Jamilatun, A. Budiman, H. Anggorowati, A. Yuliestyan, and Y. Surya, "Ex-Situ Catalytic Upgrading of *Spirulina platensis* Residue Oil Using Silica Alumina Catalyst," vol. 9, no. 4, 2019.
- [67] J. Grams, "Catalyst Stability — Bottleneck of Efficient Catalytic Pyrolysis," 2021.
- [68] H. Shafaghat *et al.*, "In-situ catalytic pyrolysis of lignin in a bench-scale fixed bed pyrolyzer," *J. Ind. Eng. Chem.*, vol. 54, pp. 447–453, 2017, doi: 10.1016/j.jiec.2017.06.026.
- [69] C. Geun, X. Meng, Y. Pu, and A. J. Ragauskas, "Bioresource Technology The critical role of lignin in lignocellulosic biomass conversion and recent pretreatment strategies: A comprehensive review," *Bioresour. Technol.*, vol. 301, no. November 2019, p. 122784, 2020, doi: 10.1016/j.biortech.2020.122784.

- [70] V. Balasundram *et al.*, "Journal of Analytical and Applied Pyrolysis Catalytic upgrading of pyrolysis vapors over metal modified HZSM-5 via in-situ pyrolysis of sugarcane bagasse : Effect of nickel to cerium ratio on," vol. 134, no. June, pp. 309–325, 2018, doi: 10.1016/j.jaap.2018.06.021.