

BIO-OIL AND BIO-HYDROGEN PRODUCTION USING RED MUD CATALYST FROM OIL PALM BIOMASS WASTE

ARIF HIDAYAT^{1*}; CHOLILA TAMZYSI¹ and MUFLIH ARISA ADNAN¹

ABSTRACT

Indonesia produces solid waste from oil palm plantations that have the potential to produce bio-oil and bio-hydrogen in the context of sustainable energy development. This article reports on the utilisation of biomass as bio-oil and bio-hydrogen producer by catalytic pyrolysis using solid waste from the aluminium industry as a catalyst. Catalytic pyrolysis was carried out in a fixed-bed reactor with varying temperatures. Three types of oil palm biomass were subjected to pyrolysis and catalytic pyrolysis to obtain hydrogen-rich gas products at various temperatures and flow rates. The products were characterised using gas chromatography-mass spectrometry (GC-MS). The results showed that the yields of bio-oil and bio-hydrogen obtained from oil palm biomass varied in the range of 18–40 wt% and 23–37 wt% respectively. The liquid product from catalytic pyrolysis of palm biomass using red mud (RM) catalyst contains primary oxygenate compounds such as acids, aromatics and esters.

Keywords: biomass waste, bio-hydrogen, bio-oil, oil palm, red mud.

Received: 26 December 2023; **Accepted:** 24 October 2024; **Published online:** 7 January 2025.

INTRODUCTION

The oil palm industry produces abundant biomass waste, both solid and liquid waste. Oil palm plantations globally generate over 300 million tonnes of annual waste. The oil palm plantation generates solid waste, including biomass residues such as trunks and fronds. Meanwhile, palm kernel shells and fibre are by-products of the milling process. The oil palm plantations produced a total of 75% of biomass waste which is mostly left to rot in the plantations for composting and fertilisation purposes such as for mulching and nutrient recovery, while the remaining 25% is from the milling process (including empty fruit bunches, kernel shells and fibre) (Dungani et al., 2018). Direct combustion of biomass waste can generate energy.

Lignocellulosic biomass, an abundant renewable resource can be efficiently converted into energy

and various chemicals at biorefinery facilities. Oil palm trunks are biomass produced from replanting activities after oil palm reaches an economic age of 20–25 years. Production of hydrogen from the oil palm biomass is a breakthrough procedure as it can lower deforestation rates and preserve the environment. Oil palm trunks are available abundantly because oil palm plantations replant when oil palm trees are no longer productive (Loh, 2017).

The frond consists of a mature leaf and a leaf stem, which produces leaflets. The fronds are left to rot in the oil palm plantation area. The oil palm plantation produces approximately 11 t of fronds per hectare after the harvest containing around 44%–45% cellulose, 23%–24% hemicellulose and 17%–18% lignin. The physical and chemical properties of oil palm fronds and trunks are influenced by plant age, planting location and soil conditions. Oil palm plantations will experience a decline in fruit yield and oil production after 25 years. Therefore, the plantation management replants the oil palm and leaves the trunk as biomass waste. In general, 1 ha of oil palm plantation can

¹ Chemical Engineering Department, Universitas Islam Indonesia, Yogyakarta 55188, Indonesia.

* Corresponding author e-mail: arif.hidayat@uii.ac.id

generate around 75 t of trunks. The trunk contains high levels of lignocellulosic substances such as cellulose, hemicellulose and lignin (Loh, 2017).

Gasification, pyrolysis and supercritical processes are thermo-chemical techniques performed on biomass involving a series of chemical reactions to produce liquid, gaseous and solid products (Ong et al., 2020). Pyrolysis is a thermo-chemical conversion method in the absence of oxygen (O) and releases the embodied energy of biomass. The main gaseous pyrolysis products are hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). Thermal gasification of biomass produces gas that contains synthesis gas in addition to charcoal and tar. The main composition of the synthesis gas is CO and H_2 with small amounts of CO, N_2 , CH_4 and H_2O . The composition varies depending on the type of feedstock, gasification method, operating conditions etc. The percentage of hydrogen yield in synthesis gas can be increased by applying water gas shift (WGS) technology using an appropriate catalyst. Several types of catalysts including zeolite, carbon, metal oxide, alumina and silica have been reported for reforming and improving biomass pyrolysis vapour. The catalytic properties of these different types of catalysts were enhanced by depositing various metals, including nickel (Ni), cobalt (Co), copper (Cu), cerium (Ce), platinum (Pt), lanthanum (La), and ruthenium (Ru) (Ho & Wu, 2020; Jiang et al., 2015; Liu et al., 2020; Santamaria et al., 2020a; 2020b).

Red mud (RM) is generated from the refining of bauxite to produce alumina by the Bayer process. In the bauxite industries, the processing of 1 t of bauxite will produce 500–600 kg of RM. RM contains mostly metal oxides that can be used as catalysts in several chemical reactions (Hidayat et al., 2020, 2021). RM released into the environment will threaten environmental safety and human health such as heavy metal pollution, soil pollution and groundwater pollution. Therefore, the utilisation of RM will provide an alternative solution to the solid waste problem from the bauxite processing industry.

RM impregnated with nickel was prepared as a catalyst for ammonia decomposition. The test results showed good catalytic activity performance (Cao et al., 2014). The RM modified by embedding Ru metal showed good performance for ammonia decomposition reaction and had high catalytic efficiency and stability. The RM-based catalysts have demonstrated economic advantages and technological feasibility in the production of hydrogen. The catalytic efficiency has improved through high-temperature calcination, an acid treatment, impregnation of active metals and a reduction process (Kurtoğlu and Uzun, 2016). RM can be used for hydrogen production via steam reforming tar from biomass waste at 200°C–850°C.

Besides, catalysts with different iron (Fe) and Ce weight percentages were prepared using co-precipitation (Dulger Irtem et al., 2014; Kurtoğlu & Uzun, 2016). The RM can be modified by acid treatment followed by calcination at high temperatures (> 500°C). The tar conversion and hydrogen yield increased when the temperature increased in the non-catalytic tar steam reforming process (Das & Mohanty, 2019). The tar conversion is almost complete when operating temperatures are above 700°C. At high temperatures, hydrogen production increases by the thermal cracking of tar using steam as the gasifying agent. The addition of active metals can further enhance water gas shift reactions and steam reforming, leading to a significant increase in tar conversion and hydrogen production. The modified RM catalyst resulted in an increase in hydrogen yield compared to the Fe-Ce catalyst due to decreased activity. The reduced process efficiency was observed when modified RM was present due to its limited activity at lower steam reforming temperatures (Duman et al., 2014). The water gas shift reaction catalysed by iron oxide will be inhibited by the sodium aluminium silicate hydrate contained in the RM. Upgrading bio-oil by enhancing various long-chain hydrocarbon compounds from the pyrolysis of hemp seeds can be carried out by using RM as a catalyst at high pressure. The co-processing of bio-oil produced a bio-oil with low acidity and oxygen content.

Several catalysts such as alkali metals, transition metals, calcium-based and nickel-based have been intensively developed for hydrogen production from biomass (Adnan et al., 2017; Dang et al., 2020; Ebadi et al., 2019; Zhang et al., 2014). The physicochemical characteristics of catalysts required to support hydrogen production are high porosity, large surface area, wide pore size distribution, high activity and good thermal stability. High-activity catalysts will increase the reaction rate and enhance the yield of hydrogen production. Synthesis gas production from pyrolysis of pine wood chips catalysed by Ni/CaAlO_x has been investigated by Chen et al. (2016). The catalyst was synthesised by the co-precipitation method by varying calcium to aluminium ratio (Ca:Al). The results showed abundant hydrogen content, and the synthesis gas reached 90% by volume. CO selectivity and H_2 concentration increased with the addition of Ca to the catalyst, thereby increasing synthesis gas production. The catalyst decreased in activity due to the formation of coal deposits on the surface of the material. The bifunctional Fe/CaO catalyst can be prepared by the impregnation method (Yang et al., 2017). Catalyst activation was investigated during biomass pyrolysis which was carried out in a fixed-bed reactor consisting of two-stage. The tar catalytic cracking occurs in the presence of $Ca_2Fe_2O_5$ on the bifunctional catalyst (Valle et al., 2020). Catalytic

pyrolysis of rice husk biomass using a catalyst in a fixed bed system efficiently produced synthesis gas with high hydrogen content (Liu et al., 2020). The study found that the hydrogen production reached a maximum temperature of 800°C and a steam to carbon dioxide ratio of 0.8. The catalyst has high activity due to the good dispersion of active sites and its ability to release oxygen for carbon decomposition.

The advanced technology to produce hydrogen from biomass needs to be developed to gain renewable and sustainable energy (Sukiran et al., 2017). Natural gas which is the conventional source for hydrogen production requires a long process route, is expensive, inefficient in energy use and not environmentally friendly. Biomass is a potential and important candidate as a renewable energy source. Edible oil, which is mostly produced from oil palm fruits, is abundantly available in Indonesia. A palm oil mill generates 55 t of solid waste for every hectare of oil palm plantations. The abundant amount of solid waste requires the utilisation of palm oil solid waste to produce hydrogen by the pyrolysis process. The palm oil industry continuously maintains the productivity of yield and quality of palm fruit without opening new areas for plantation. It is necessary to replant oil palm trees by cutting down the trees that are over 20 years old to maintain sustainability. This situation will increase the amount of solid waste and provide opportunities for the utilisation of oil palm solid waste for various applications including renewable energy. Pyrolysis of oil palm solid waste can produce bio-oil and bio-hydrogen which will reduce the negative impacts of waste disposal. Utilisation of palm solid waste as a renewable energy source would create a carbon-neutral process and be more environmentally friendly due to low sulphur (S) and nitrogen (N) content.

Based on the literature search, it is still rare for palm oil solid waste pyrolysis research to produce hydrogen and bio-oil using the pyrolysis process using RM as a catalyst. This study aims to study the production of bio-oil and bio-hydrogen using RM catalysts from oil palm/palm oil solid waste. The pyrolysis process was operated under different operating conditions (catalyst concentration, temperature and catalyst addition), to obtain a higher yield of hydrogen and bio-oil.

MATERIALS AND METHODS

Catalyst Preparation and Characterisation

Red mud (RM) was obtained from the bauxite refinery industry in West Kalimantan Province, Indonesia. First, the RM was ground and screened to obtain a uniform particle size. Then, the washing process is carried out using tap water. RM was dried

at 120°C for 8 hr in an oven. The RM was calcined in an electric furnace at 800°C for 2 hr. The porosity properties of RM were characterised using nitrogen gas sorption analysis. The crystalline structure was determined by X-ray diffraction (XRD) instrument.

Characterisation of the Oil Palm Biomass

The oil palm biomass was collected during the replanting at plantations of PT Perkebunan Nusantara (PTPN) XXIII, Central Kalimantan Province, Indonesia. The oil palm biomass was washed to remove any dust and impurities before being cut into pieces to reduce their size and dried in the sun until dry. The remaining moisture was removed by drying in an oven for 24 hr at 105°C. After that, the oil palm biomass was ground into small pieces using a grinder and sieved to a size of less than 1 mm. The proximate analysis was applied to calculate the content of volatile matter, fixed carbon, moisture and ash. Meanwhile, the ultimate analysis was to calculate the elemental content of oxygen (O), hydrogen (H), carbon (C), nitrogen (N), sulphur (S) and ash.

Catalytic Pyrolysis Experiments

Figure 1 shows the apparatus applied for catalytic pyrolysis of oil palm biomass using RM as a catalyst in a fixed bed system. The reactor was heated in a tubular furnace equipped with an electric heater and a thermocouple was deployed to monitor the operating temperature. The catalyst and oil palm biomass in each test were placed into the reactor. The nitrogen gas flow rate was 150 mL min⁻¹ to remove the remaining oxygen from the reactor. Gas samples were collected and analysed using a gas analyser. The liquid and solids formed were collected after the reactor reached room temperature. The liquid was analysed for the content of the constituent compounds using gas chromatography mass spectrophotometry. The functional groups were determined using Fourier transform infrared (FTIR).

RESULTS AND DISCUSSION

Catalyst Characterisation

Analysis of porosity. The porosity characteristics of materials can be predicted by analysing the nitrogen gas (N₂) isotherm adsorption-desorption curve. Figure 2 exhibits the N₂ isotherm adsorption-desorption of RM before and after activation. Based on Figure 2(a), the N₂ uptake pattern in RM before activation has type II referring to the Brunauer, Deming, Deming and Teller (BDDT) classification. In type II, N₂ absorption occurs in non-porous or

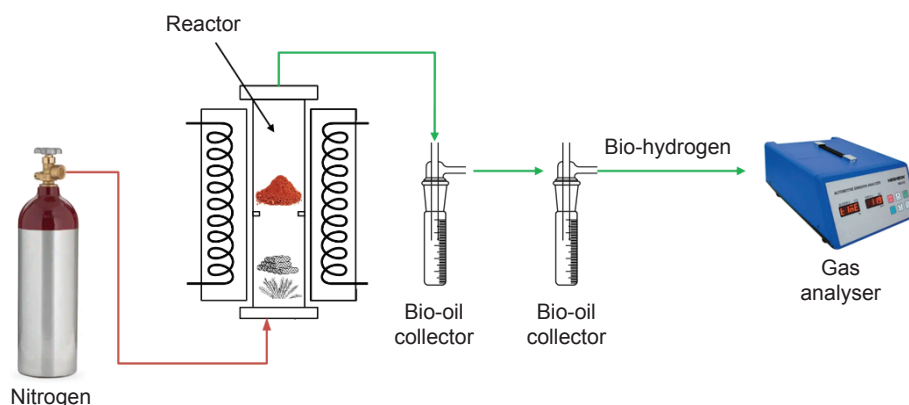


Figure 1. The catalytic pyrolysis apparatus.

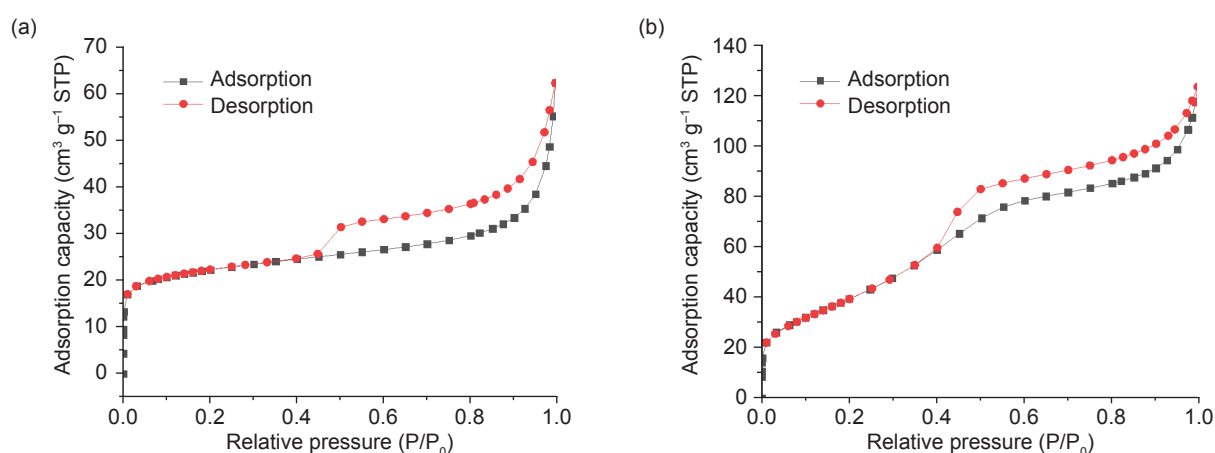


Figure 2. The nitrogen isotherm adsorption-desorption of RM (a) before and (b) after activation.

large-porous media which indicates monolayer and multilayer absorption properties. Adsorption in the monolayer occurs at a relative pressure P/P_0 smaller than 0.2. Multilayer adsorption will occur in the pores of the solid at relative pressures above 0.2. This is characterised by the slope which tends to level out until the relative pressure approaches 1.0. Generally, solids with a mixture of micropores and mesopores show an N_2 uptake pattern similar to type II with H3 or H4 type hysteresis. The H3 or H4 type hysteresis indicates that the material has lamellar or slit-shaped pores. The adsorption capacity increases significantly at relatively high pressures, which indicates the presence of mesopores in the material. As shown in Figure 2(b), the curve of RM after activation showed the existence of type IV with H1 or H3 type hysteresis, which indicates that the pores are cylindrical or lamellar.

The Brunauer-Emmett-Teller (BET) specific surface area is an important parameter of material characteristics. A catalyst that has a high surface area will provide more active sites that are anchored on the surface to enhance catalytic activity. Table 1 shows the porosity characteristics of RM before and after calcination.

TABLE 1. THE POROSITY CHARACTERISTICS OF RM BEFORE AND AFTER CALCINATION

Characteristics	RM	Activated RM
Specific surface area ($m^2 g^{-1}$)	114.53	203.04
Pore volume ($cm^3 g^{-1}$)	0.2106	0.2402
Average pore radius (\AA)	22.93	21.32

Note: RM - red mud.

Table 1 shows that the specific surface area and total pore volume increase due to the diminishing impurities in the internal pore of RM. Meanwhile, the average pore radius is reduced from 22.93–21.32 \AA . During the calcination process, new pores are likely to form due to the release of compounds on the surface at high temperatures.

Analysis of X-ray diffraction (XRD). The XRD aims to determine the mineral crystal structure content in RM (Figure 3). Based on Figure 3, the diffractogram shows the characteristic peaks, which indicate a high presence of gibbsite, the largest component contained in bauxite, followed by Al_2O_3 , hematite (Fe_2O_3), sodium oxide (Na_2O), quartz (SiO_2) and anatase (TiO_2). This means that the RM is mostly composed of the Al_2O_3

and Fe₂O₃. The RM diffractogram patterns do not show significant differences between before and after calcination. The mineral from the RM does not decompose significantly after the calcination process. This can be due to the favourable calcination process of RM before and after activation in opening the pores (Dong et al., 2023; Liu et al., 2023).

Chemical composition. The X-ray fluorescence (XRF) results in Table 2 confirmed that the RM sample contained several metal oxides and alkali metals impurities such as Na₂O and SiO₂, with percentages of 17.39% and 10.3% respectively. Trace components of impurities were also detected such as phosphorus (P), magnesium (Mg), calcium (Ca), potassium (K) and titanium (Ti). The unusual amount of Al₂O₃ in this RM sample was so high as compared to other worldwide refinery plants which commonly ranged from 14%–28%. In ratio, the iron to aluminium ratio (Fe:Al) was calculated at 0.34 while the other impurities ratio (Fe:Na and Fe:Si) are at 1.02 and 1.72 respectively. There was a slight change in the chemical composition of milled RM which assumed would not affect the reaction.

Characterisation of the Palm Oil Trunks

Based on Table 3, the composition of oil palm biomass comprises lignin, hemicellulose, and cellulose. Compared to fossil fuels, oil palm biomass has a lower N content (less than 1% mass), S content (less than 0.2% mass) and O content (40%–50% mass). The quality of bio-oil is influenced by the variation in the physicochemical properties of biomass feedstock.

A higher cellulose content from oil palm biomass is needed to achieve a high production efficiency of liquid products (bio-oil). Decomposition of cellulose components produces more volatile matter which can be condensed into bio-oil during pyrolysis. The empty fruit bunches have the highest cellulose content (59.70% mass) followed by the trunk (34.50 wt%), and fronds (20.80% mass).

The proximate analysis showed a low water content (< 10 wt%) which is affordable as feedstock for the pyrolysis process. The water content in raw materials influences the yields and bio-oil quality. The heat required for pyrolysis will increase when the biomass used has a high moisture content because extra heat is needed to evaporate the water

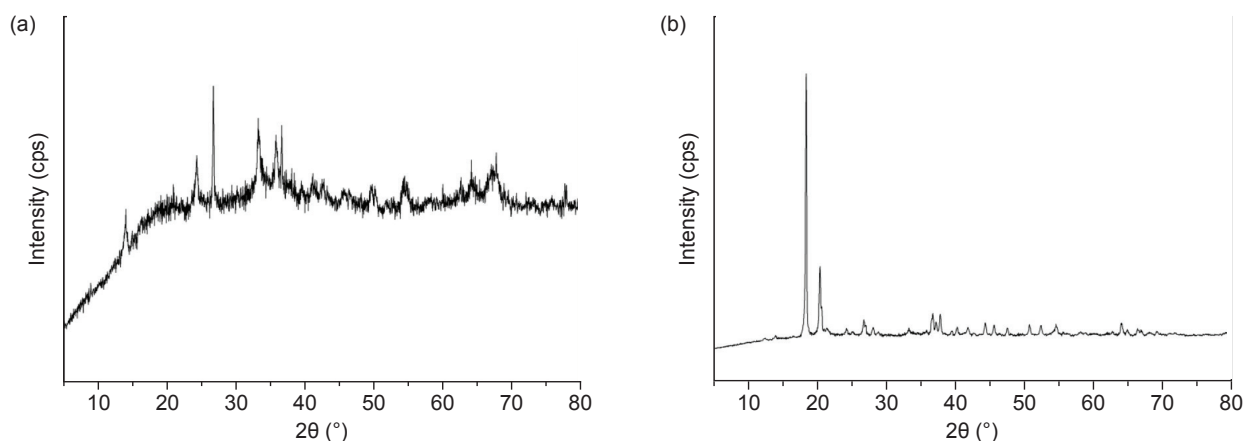


Figure 3. X-ray diffraction (XRD) analysis of red mud (RM): (a) raw RM and (b) after calcination.

TABLE 2. CHEMICAL COMPOSITION OF RED MUD (RM) BEFORE AND AFTER CALCINATION OBTAINED BY XRF

Sample	Major component (%)					Ratio		
	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	SiO ₂	TiO ₂	Fe:Al	Fe:Na	Fe:Si
RM Parent	51.8	17.73	17.39	10.3	1.67	0.34	1.02	1.72
RM 8 hr-mill	49.47	17.60	17.45	11.93	1.55	0.36	1.01	1.48

Note: RM - red mud; Al₂O₃ - Aluminium oxide; Fe₂O₃ - hematite; Na₂O - sodium oxide; SiO₂ - quartz; TiO₂ - anatase.

TABLE 3. ANALYSIS OF THE COMPONENT OF OIL PALM BIOMASS

Type of biomass	Cellulose (% mass)	Hemicellulose (% mass)	Lignin (% mass)
Trunks	59.70	22.10	18.20
Fronds	40.00	20.00	30.00
Empty fruit bunches	34.50	31.80	25.70

vapour and increase the temperature of the vapour to the setting temperature. Therefore, pyrolysis using feedstock containing a high-water content will provide bio-oil with a high-water content with more energy consumption during the pyrolysis. In the pyrolysis process, higher volatile matter content in biomass is favourable for bio-oil production. The bio-oil formation reaction is dependent on the content of volatile materials. Meanwhile, the fixed carbon content is the element that can be transformed into char. Biomass with high fixed carbon content is favoured to produce charcoal. The ash content of the fronds is lower than that of empty fruit bunches and trunks. Low biomass ash content will improve the quality and quantity of bio-oil by avoiding secondary reactions from condensed steam and reducing solid content in bio-oil (Stefanidis et al., 2015).

The elemental analysis shows that the contents of C, H, O, N and S in oil palm trunks, fronds and empty fruit bunches are in the range of 43.00%–52.00%, 6.00%–7.00%, 40.00%–50.00%, 0.20%–0.70% and 0.00%–0.16% mass. The relatively high C and H content provides a higher heating value (HHV). The oxygen content in the biomass should be low during the pyrolysis process because the oxygen will be bound to the hydrocarbon molecules as oxygenated compounds to reduce the quality of the bio-oil. Meanwhile, biomass pyrolysis with high oxygen content tends to produce bio-oil with high water content. The formation of aromatic compounds in bio-oil can be enhanced by the presence of C and H atoms in biomass. Low S and N content in biomass would prevent the formation of SO_x and NO_x (Abu Bakar & Titiloye, 2013).

Thermogravimetric analysis (TGA) of trunks, fronds and empty fruit bunches of oil palm is to observe the thermal decomposition pattern, and the results are presented in Figure 4. The thermal decomposition covers three stages due to the different lignocellulosic components. The first stage takes place at the temperature range of 50°C–120°C where the mass of biomass decreases slightly due to evaporation of water content. The second stage occurs at the temperature range of 120°C–250°C where the mass of palm oil biomass is relatively constant as the amount of light volatile matter that evaporates is relatively low. The biomass receives most of the heat energy supplied to it to raise the temperature. The following step is the primary thermal breakdown of oil palm biomass, which takes place at temperatures between 250°C and 500°C. The major volatile organic matter (hemicellulose and cellulose) undergoes a decomposition process to become condensable or non-condensable gas. In the final stage at temperatures above 500°C, thermal degradation of biomass occurs slowly due to lignin decomposition. The thermal decomposition pattern of palm biomass

is consistent with the results of proximate analysis. Thermal degradation of hemicellulose primarily occurs in the temperature range of 220°C–350°C, accompanied by the degradation of cellulose in the temperature ranging from 325°C–400°C (Wang et al., 2022).

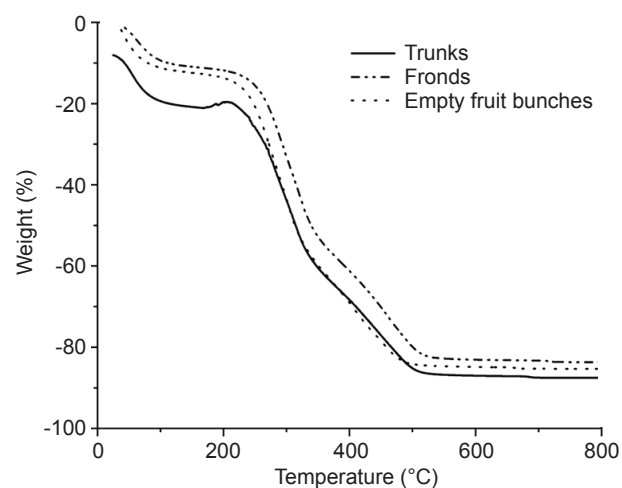


Figure 4. Thermogravimetric analysis (TGA) of oil palm biomass waste (trunks, fronds and empty fruit bunches).

Catalytic Pyrolysis Experiments

Effect of the addition of RM on distribution of pyrolysis products. To determine the effect of the addition of RM on the pyrolysis of palm biomass, pyrolysis experiments were conducted as shown in Figure 5. Both catalytic and non-catalytic pyrolysis show the same trend i.e., the percentage of liquid and gas increases with the increase of pyrolysis temperature. Meanwhile, the percentage of solid products reduces with increasing temperature. The gas yield in catalytic pyrolysis is higher than in non-catalytic pyrolysis, implying that the addition of a catalyst contributes to the addition of gas products during the pyrolysis process. While the solid product does not have a significant difference between non-catalytic and catalytic pyrolysis.

Effect of temperature on distribution of catalytic pyrolysis products. The distribution of catalytic pyrolysis products obtained from the pyrolysis of trunks, fronds, and empty fruit bunches at different temperatures can be seen in Figure 6. The yield of liquid, char and gas products from pyrolysis at 400°C, 500°C and 600°C is in the range of 21.21–36.85, 10.75–25.40 and 41.60–68.05 wt% respectively. The type of oil palm or palm oil biomass and pyrolysis temperature affects the product yields. Pyrolysis of oil palm fronds provides higher liquid yields than from empty fruit bunches and trunks. The highest amount of charcoal was obtained from

the pyrolysis of empty fruit bunches. Pyrolysis of biomass with high volatile matter and low ash content produces large amounts of liquid products. The yield of pyrolysis products is in accordance with the lignocellulosic content of the biomass reported by Lu and Gu (2022).

Based on Table 4, empty fruit bunches have high hemicellulose and cellulose content but low lignin and extractives content. Thus, pyrolysis of empty fruit bunches provides the highest amount of liquid product. Increasing the pyrolysis temperature has a small influence on the yield of products

obtained from the trunks and empty fruit bunches. It is because most of the components of oil palm trunks and empty fruit bunches are cellulose and hemicellulose which can decompose completely at temperatures below 500°C. However, increasing the pyrolysis temperature for fronds affects product yields, especially liquid products because they contain high levels of lignin, which can decompose over a wide temperature range of 200°C–900°C. The biochar yield decreased with increasing pyrolysis temperature due to greater primary decomposition of biomass (Claoston et al., 2014).

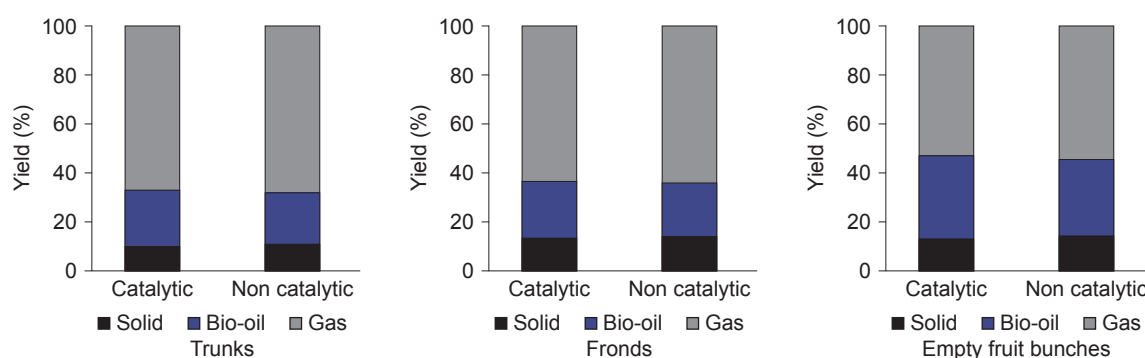


Figure 5. Effect of red mud (RM) catalyst on distribution of pyrolysis products.

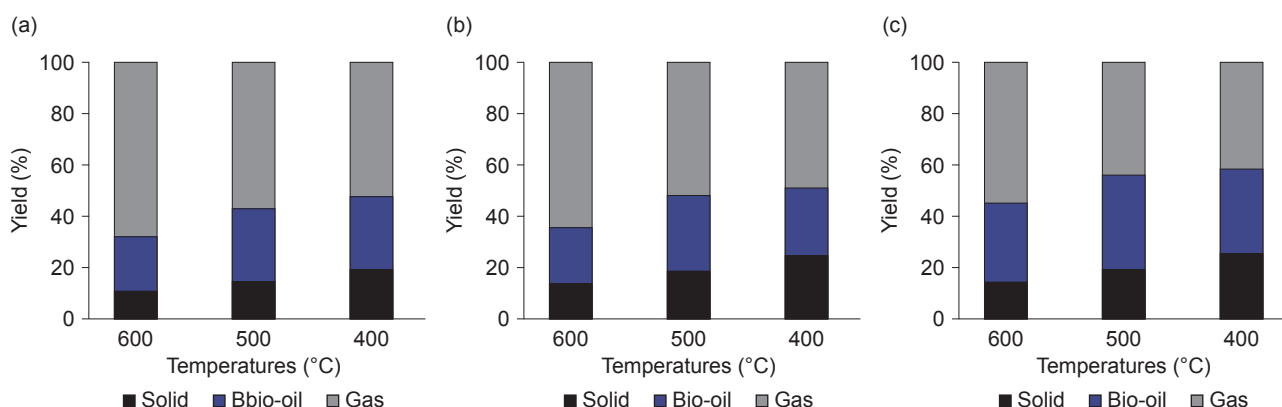


Figure 6. Effect of temperature on distribution of catalytic pyrolysis products from oil palm biomass waste: (a) trunks, (b) fronds and (c) empty fruit bunches.

TABLE 4. PROXIMATE AND ULTIMATE ANALYSIS OF OIL PALM BIOMASS WASTE

Analysis proximate (% mass)	Percentage (% mass)		
	Trunks	Fronds	Empty fruit bunches
Moisture	7.60	7.50	7.38
Volatile matter	74.06	73.06	76.41
Fixed carbon	14.92	16.55	11.57
Ash	3.42	2.89	4.64
Analysis ultimate (% mass)	Percentage (% mass)		
	Trunks	Fronds	Empty fruit bunches
Carbon	43.68	43.44	51.77
Hydrogen	6.07	6.08	7.04
Oxygen	49.84	50.28	40.31
Sulphur	0.40	0.19	0.72
Nitrogen	0.0	0.01	0.16

Effect of catalyst concentration on distribution of pyrolysis products. The concentration of catalyst was varied from 5% to 15% in order to study the impact of varying the catalyst concentration on the distribution of catalytic pyrolysis products. Figure 7 shows the effect of catalyst concentration on distribution of pyrolysis products. As shown in Figure 7, the liquid yield increases as the catalyst concentration increases. Increasing the amount of RM catalyst leads to the cracking rate of non-volatile oligomeric compounds into monomers, thus promoting the yield of volatile products which will be condensed into liquid. The bio-char yield decreases with the increase of catalyst concentration. An increase in temperature will generate more carbon monoxide (CO) and hydrogen (H₂) which consequently reduces the yield of the solid product. The decrease in bio-char yield can be explained as the decomposition of tar formed during pyrolysis into gaseous and liquid products.

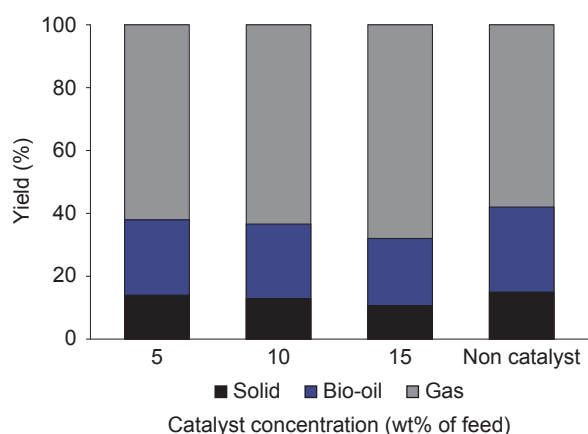


Figure 7. Effect of catalyst concentration on distribution of pyrolysis products from oil palm trunk biomass waste.

Composition of Liquid Products from Catalytic Pyrolysis of Oil Palm Biomass

Table 5 shows the liquid product compounds produced from the empty fruit bunches, trunks, and fronds of oil palm at the temperature of 500°C. Based on GC-MS analysis, oxygenated compounds are the main composition present in the liquid product such as acids, aromatics, phenols, aldehydes, ketones, alcohols and esters. The high content of these compounds contributes to the low calorific value of the liquid product. The composition of the compounds contained in the liquid product depends on the type of oil palm biomass and its constituent atoms, especially the lignocellulosic components. The biomass composition greatly influences the compounds in bio-oil or liquid products. The decomposition of cellulose and hemicellulose into anhydrosugars and heterocyclic compounds such as furan and furan derivatives and acetic acid. The lignin fraction of biomass undergoes devolatilisation resulting in oxygenated aromatic compounds such as phenol and phenolic derivatives. Besides lignin content, biomass alkaline mineral metals will influence the content of the liquid product (Bensidhom et al., 2021).

Gas Product Distribution from Catalytic Pyrolysis of Oil Palm Biomass Waste

Figure 8 presents the main composition of the gas product from pyrolysis of oil palm biomass waste. It can be seen from the table that the pyrolysis gas products obtained contain low hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane (CH₄) components. Gas products resulting

TABLE 5. COMPOUND COMPOSITION OF LIQUID PRODUCTS FROM OIL PALM BIOMASS WASTE

Compound	Composition (%)		
	Trunks	Fronds	Empty fruit bunches
Furan, 2,5-diethoxytetrahydro-	0.17	0.22	0.24
Furan, 2-ethyl-	0.07	0.05	0.04
Acetic acid	13.39	0.32	14.49
2-Furan-carboxaldehyde	4.41	6.63	3.34
2-Furanethanol	-	-	1.78
3-Furanethanol	2.93	1.23	-
Phenol	9.32	8.17	3.32
Phenol, 2-methoxy-	1.65	2.23	2.78
Phenol, 2,6-demethoxy-	2.96	0.11	3.85
Phenol, 2,6-demethoxy-4-(2-propenyl)-	0.15	0.13	0.28
2-Propanone, 1-hydroxy-	6.69	5.36	4.65
4-Propyl-syringol	0.10	0.10	0.15
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.61	0.52	0.35
Octanoic acid	-	-	0.33
Benzenemethanol	-	0.63	0.43
3,5-Dimethoxy-4-hydroxytoluene	1.01	1.18	1.88
Benzene, 1,2,3-trimethoxy-5-methyl-	-	0.54	-
Benzaldehyde, 4-hydroxy-3-methoxy-	0.10	0.29	0.42
2-Methoxy-4-vinylphenol	0.21	-	0.46
2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	0.08	0.06	0.15

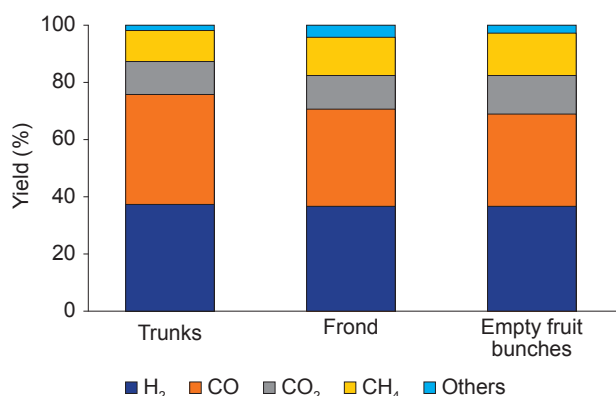


Figure 8. Gas product distribution from catalytic pyrolysis of oil palm biomass waste.

from pyrolysis from oil palm trunks contain higher concentrations of H₂, CO, CO₂ and CH₄ compared to products obtained from oil palm fronds and empty fruit bunches. Oil palm trunks contain high levels of cellulose and hemicellulose but low levels of lignin. Cellulose and hemicellulose can decompose and be released as vapour at lower temperatures compared to lignin. Empty fruit bunches contain high levels of lignin so the pyrolysis gas produced is low (Sembiring et al., 2015).

CONCLUSION

The three types of oil palm biomass can produce bio-oil and bio-hydrogen as a renewable energy source by pyrolysis process using catalysts from RM. The yield of liquid and gaseous pyrolysis product increases as temperature increases. The addition of catalyst also promotes the increase of liquid and gas pyrolysis products yield. Based on GC-MS analysis, the presence of RM catalyst enhanced the amounts of hydrocarbons in bio-oils. The results showed that the liquid product from catalytic pyrolysis of palm biomass using RM catalyst contains primary oxygenated compounds such as acids, aromatics and esters. RM is a solid waste and is widely available, therefore it is a plausible alternative to be produced on an industrial scale. RM catalysts were tested for catalytic pyrolysis of oil palm biomass under different operating conditions. The RM catalyst showed good activity to produce higher bio-oil yields.

ACKNOWLEDGEMENT

This research financial support was provided by Direktorat Jenderal Pendidikan Tinggi, Riset dan Teknologi, Kementerian Pendidikan, Kebudayaan, Riset dan Teknologi Republik Indonesia.

REFERENCES

- Abu Bakar, M. S., & Titiloye, J. O. (2013). Catalytic pyrolysis of rice husk for bio-oil production. *Journal of Analytical and Applied Pyrolysis*, 103, 362–368. <https://doi.org/10.1016/j.jaap.2012.09.005>
- Adnan, M. A., Muraza, O., Razzak, S. A., Hossain, M. M., & de Lasa, H. I. (2017). Iron oxide over silica-doped alumina catalyst for catalytic steam reforming of toluene as a surrogate tar biomass species. *Energy & Fuels*, 31(7), 7471–7481. <https://doi.org/10.1021/acs.energyfuels.7b01301>
- Bensidhom, G., Arabiourrutia, M., Trabelsi, A. B. H., Cortazar, M., Ceylan, S., & Olazar, M. (2021). Fast pyrolysis of date palm biomass using Py-GCMS. *Journal of the Energy Institute*, 99, 229–239. <https://doi.org/10.1016/j.joei.2021.09.012>
- Cao, J. L., Yan, Z. L., Deng, Q. F., Wang, Y., Yuan, Z. Y., Sun, G., Jia, T. K., Wang, X. D., Bala, H., & Zhang, Z. Y. (2014). Mesoporous modified-red-mud supported Ni catalysts for ammonia decomposition to hydrogen. *International Journal of Hydrogen Energy*, 39(11), 5747–5755. <https://doi.org/10.1016/j.ijhydene.2014.01.169>
- Chen, F., Wu, C., Dong, L., Vassallo, A., Williams, P. T., & Huang, J. (2016). Characteristics and catalytic properties of Ni/CaAlO_x catalyst for hydrogen-enriched syngas production from pyrolysis-steam reforming of biomass sawdust. *Applied Catalysis B: Environmental*, 183, 168–175. <https://doi.org/10.1016/j.apcatb.2015.10.028>
- Claoston, N., Samsuri, A., Ahmad Husni, M., & Mohd Amran, M. (2014). Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste Management & Research*, 32(4), 331–339. <https://doi.org/10.1177/0734242X14525822>
- Dang, C., Liu, L., Yang, G., Cai, W., Long, J., & Yu, H. (2020). Mg-promoted Ni-CaO microsphere as bi-functional catalyst for hydrogen production from sorption-enhanced steam reforming of glycerol. *Chemical Engineering Journal*, 383, Article 123204. <https://doi.org/10.1016/j.cej.2019.123204>
- Das, B., & Mohanty, K. (2019). A review on advances in sustainable energy production through various catalytic processes by using catalysts derived from waste red mud. *Renewable Energy*, 143, 1791–1811. <https://doi.org/10.1016/j.renene.2019.05.114>

- Dong, W., Li, S., Wang, M., Yuan, X., Cao, Y., & Ao, X. (2023). Nickel-loaded red mud catalyst for steam gasification of bamboo sawdust to produce hydrogen-rich syngas. *International Journal of Hydrogen Energy*, 48(57), 21624–21635. <https://doi.org/10.1016/j.ijhydene.2023.03.064>
- Dulger Irdem, S., Parparita, E., Vasile, C., Uddin, M. A., & Yanik, J. (2014). Steam reforming of tar derived from walnut shell and almond shell gasification on red mud and iron-ceria catalysts. *Energy & Fuels*, 28(6), 3808–3813. <https://doi.org/10.1021/ef500238f>
- Duman, G., Uddin, M. A., & Yanik, J. (2014). Hydrogen production from algal biomass via steam gasification. *Bioresource Technology*, 166, 24–30. <https://doi.org/10.1016/j.biortech.2014.04.096>
- Dungani, R., Aditiawati, P., Aprilia, S., Yuniarti, K., Karliati, T., Suwandhi, I., & Sumardi, I. (2018). Biomaterial from oil palm waste: Properties, characterization and applications. In V. Waisundara (Ed.), *Palm oil* (pp. 31–52). IntechOpen. <https://doi.org/10.5772/intechopen.76412>
- Ebadi, A. G., Hisoriev, H., Zarnegar, M., & Ahmadi, H. (2019). Hydrogen and syngas production by catalytic gasification of algal biomass (*Cladophora glomerata* L.) using alkali and alkaline-earth metals compounds. *Environmental Technology*, 40(9), 1178–1184. <https://doi.org/10.1080/09593330.2017.1417495>
- Hidayat, A., Adnan, M. A., & Chafidz, A. (2021). Synthesis dimethyl ether from methanol using red mud catalyst. *Materials Science Forum*, 1029, 147–152. <https://doi.org/10.4028/www.scientific.net/MSF.1029.14>
- Hidayat, A., Roziq, G. K., Muhammad, F., Kurniawan, W., & Hinode, H. (2020). Biodiesel synthesis from used cooking oil using red mud as heterogeneous catalyst. *Materials Science Forum*, 991, 144–149. <https://doi.org/10.4028/www.scientific.net/MSF.991.144>
- Ho, M. C., & Wu, T. Y. (2020). Sequential pretreatment with alkaline hydrogen peroxide and choline chloride: Copper (II) chloride dihydrate – Synergistic fractionation of oil palm fronds. *Bioresource Technology*, 301, 122684. <https://doi.org/10.1016/j.biortech.2019.122684>
- Jiang, L., Hu, S., Wang, Y., Su, S., Sun, L., Xu, B., He, L., & Xiang, J. (2015). Catalytic effects of inherent alkali and alkaline earth metallic species on steam gasification of biomass. *International Journal of Hydrogen Energy*, 40(45), 15460–15469. <https://doi.org/10.1016/j.ijhydene.2015.08.111>
- Kurtoğlu, S. F., & Uzun, A. (2016). Red mud as an efficient, stable and cost-free catalyst for CO_x-free hydrogen production from ammonia. *Scientific Reports*, 6(1), Article 32279. <https://doi.org/10.1038/srep32279>
- Liu, C., Chen, D., Cao, Y., Mao, Y., Wang, W., Wang, Z., & Kawi, S. (2020). Catalytic steam reforming of *in-situ* tar from rice husk over MCM-41 supported LaNiO₃ to produce hydrogen rich syngas. *Renewable Energy*, 161, 408–418. <https://doi.org/10.1016/j.renene.2020.07.089>
- Liu, K., Wei, G., Zhu, Y., Zhang, L., & He, Z. (2023). A clean route of biodiesel production using red mud-based potassium catalyst. *Journal of Environmental Chemical Engineering*, 11(5), Article 111015. <https://doi.org/10.1016/j.jece.2023.111015>
- Loh, S. K. (2017). The potential of the Malaysian oil palm biomass as a renewable energy source. *Energy Conversion and Management*, 141, 285–298. <https://doi.org/10.1016/j.enconman.2016.08.081>
- Ong, H. C., Chen, W. H., Singh, Y., Gan, Y. Y., Chen, C. Y., & Show, P. L. (2020). A state-of-the-art review on thermochemical conversion of biomass for biofuel production: A TG-FTIR approach. *Energy Conversion and Management*, 209, Article 112634. <https://doi.org/10.1016/j.enconman.2020.112634>
- Santamaria, L., Arregi, A., Lopez, G., Artetxe, M., Amutio, M., Bilbao, J., & Olazar, M. (2020a). Effect of La₂O₃ promotion on a Ni/Al₂O₃ catalyst for H₂ production in the in-line biomass pyrolysis-reforming. *Fuel*, 262, Article 116593. <https://doi.org/10.1016/j.fuel.2019.116593>
- Santamaria, L., Artetxe, M., Lopez, G., Cortazar, M., Amutio, M., Bilbao, J., & Olazar, M. (2020b). Effect of CeO₂ and MgO promoters on the performance of a Ni/Al₂O₃ catalyst in the steam reforming of biomass pyrolysis volatiles. *Fuel Processing Technology*, 198, Article 106223. <https://doi.org/10.1016/j.fuproc.2019.106223>
- Sembiring, K. C., Rinaldi, N., & Simanungkalit, S. P. (2015). Bio-oil from fast pyrolysis of empty fruit bunch at various temperature. *Energy Procedia*, 65, 162–169. <https://doi.org/10.1016/j.egypro.2015.01.052>

- Stefanidis, S. D., Heracleous, E., Patiaka, D. T., Kalogiannis, K. G., Michailof, C. M., & Lappas, A. A. (2015). Optimization of bio-oil yields by demineralization of low quality biomass. *Biomass and Bioenergy*, 83, 105–115. <https://doi.org/10.1016/j.biombioe.2015.09.004>
- Sukiran, M. A., Abnisa, F., Daud, W. M. A. W., Bakar, N. A., & Loh, S. K. (2017). A review of torrefaction of oil palm solid wastes for biofuel production. *Energy Conversion and Management*, 149, 101–120. <https://doi.org/10.1016/j.enconman.2017.07.011>
- Valle, B., García-Gómez, N., Remiro, A., Bilbao, J., & Gayubo, A. G. (2020). Dual catalyst-sorbent role of dolomite in the steam reforming of raw bio-oil for producing H₂-rich syngas. *Fuel Processing Technology*, 200, 106316. <https://doi.org/10.1016/j.fuproc.2019.106316>
- Wang, Y., Akbarzadeh, A., Chong, L., Du, J., Tahir, N., & Awasthi, M. K. (2022). Catalytic pyrolysis of lignocellulosic biomass for bio-oil production: A review. *Chemosphere*, 297, 134181. <https://doi.org/10.1016/j.chemosphere.2022.134181>Get rights and content
- Yang, S., Zhang, X., Chen, L., Sun, L., Xie, X., & Zhao, B. (2017). Production of syngas from pyrolysis of biomass using Fe/CaO catalysts: Effect of operating conditions on the process. *Journal of Analytical and Applied Pyrolysis*, 125, 1–8. <https://doi.org/10.1016/j.jaap.2017.05.007>
- Zhang, Y., Gong, X., Zhang, B., Liu, W., & Xu, M. (2014). Potassium catalytic hydrogen production in sorption-enhanced gasification of biomass with steam. *International Journal of Hydrogen Energy*, 39(9), 4234–4243. <https://doi.org/10.1016/j.ijhydene.2014.01.015>