





#### Original Research Paper

# Investigation of yields and qualities of pyrolysis products obtained from oil palm biomass using an agitated bed pyrolysis reactor

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#### HIGHLIGHTS

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>Oil palm trunk, oil palm fronds and oil palm shell were pyrolyzed by an agitated bed reactor.

 Yields and qualities of the liquid product, biochar, and gas were determined and analyzed.
 Water content, pH, density, elemental

compositions, and compounds of the liquid product were determined.

 Biochar had superior fuel properties and potential for future applications as indicated by SEM and BET.
 Pyrolysis gas contained a low concentration of combustible components.

#### GRAPHICAL ABSTRACT



## ABSTRACT

Oil palm biomass is a non-woody lignocellulosic biomass that has a high potential at the south of Thailand for biofuels and bioenergy applications. Pyrolysis of oil palm biomass to produce biofuels such as bio-oil, biochar, and pyrolysis gas is still challenging. The aim of this study was therefore to investigate the yields and qualities of pyrolysis products obtained from oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) using an agitated bed pyrolysis reactor. These biomasses were pyrolyzed at pyrolysis temperatures of 400, 450, and 500°C while the other operating parameters were fixed. The results showed that the different types of oil palm biomass and pyrolysis temperatures affected the product yields and qualities. The OPF pyrolyzed at 500°C provided the highest liquid yield. The liquid product contained a relatively high water content with a low pH value, leading to highly-oxygenated compounds as indicated by gas chromatography-electron ionization/mass spectroscopy technique (GC-EI/MS). The higher heating value (HHV) of the liquid product was 18.95-22.52 MJ/kg. The biochar had a protus structure surface with a surface area of 1.15-4.43 m<sup>2</sup>/g as indicated by BET. The pyrolysis gas contained a low Composition of combustible gases, leading to a low HHV.

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#### 1. Introduction

The applications of biomass for biofuels and bioenergy are gaining interest worldwide, as fossil fuels such as crude oil, coal, and natural gas face depletion as a result of the ever-growing demands (BP, 2019). Reliance on fossil fuels also creates negative environmental impacts, which contribute to global warming and climate change. The global consumption of fossil fuels not only impacts the environment but also poses a risk to energy systems in terms of both energy security and energy sustainability, particularly in the countries that need to import fossil fuels (Rathore et al., 2016). In light of these concerns, many countries, both developed and developing, are looking to overcome these issues by searching and innovating renewable energy resources. There are many sources of renewable energy (RE) and alternative energy (AE), including wind, hydro, solar, geothermal, wave, and biomass. Biomass is one of the main renewable energy resources that is already being widely used around the world (WBA, 2018; BP, 2019). However, the potentiality of biomass in each country or region depends on a variety of factors, such as location, climate, weather, available local plantations, agricultural activity, and industrial processing.

Thailand is home to many agro-industries, which leads to the presence of various types of biomass. The crops and plants that are available in Thailand include rice, cassava, sugar cane, corn, rubber trees, and oil palm trees. The harvesting, processing, and replanting of these crops and plants provide many forms of biomasses such as rice straw, rice husk, cassava stalk, cassava roots, corn stalk and leaves, rubberwood, and oil palm biomass (Yokoyamaa et al., 2000). In 2018, the plantation area of oil palm trees in Thailand was 0.88 million ha (Agricultural Statistics of Thailand, 2018). Most of Thailand's oil palm trees are grown in the south of the country. The harvesting and processing of fresh fruit bunches (FFB) from these trees, as well as the replantation of oil palm trees, generate a large amount of oil palm biomass. The harvesting of FFB from each oil palm tree generates two or three oil palm fronds (OPF) with leaves. Generally, the OPF and leaves are left in oil palm fields to break down into organic fertilizer for oil palm trees. The oil palm biomass generated from the processing of the FFB includes empty fruit bunches (EFB), oil palm kernel shells, oil palm fiber, and oil palm decanter (Prasertsan and Prasertsan, 1996; Yusoff, 2006; Shuit et al., 2009; Sulaiman et al., 2011; Loh, 2016). The replantation of oil palm trees also generates a large source of biomass in the form of oil palm trunks (OPT), OPF with leaves, and oil palm roots (OPR). Based on a report by the Department of Alternative Energy Development and Efficiency (DEDE), Ministry of Energy of Thailand, some of this oil palm biomass is used as biofuels for heat and power generation (DEDE, 2019). Nevertheless, it stresses that EFB, OPT, oil palm shell (OPS), OPF, and OPR hold high potentials for further exploitation for biofuels and bioenergy applications.

The conversion of biomass into biofuels or bioenergy can be performed through several processes, such as mechanical (chopping, palletization, and briquetting), thermochemical (combustion, gasification, pyrolysis, and torrefaction) and biochemical (fermentation and anaerobic digestion) conversion processes (Demirbaş, 2001; McKendry, 2002; Bridgwater, 2012; Tanger et al., 2013; Ranisau et al., 2016; Yelmen et al., 2016; Tursi, 2019). The criteria for choosing the most favorable biomass conversion process from these options are various including the type of biomass (solid, liquid or mixed sample), the biomass properties and characteristics, the desired energy product and utilization, conversion costs, as well as storage and transportation considerations. This is due to the fact that the conversion of biomass through these processes provides different types and forms of biofuels or bioenergy. Pyrolysis is one of the thermochemical conversion processes that can be used for converting biomass into biofuels, including bio-oil, biochar, and pyrolysis gas. The advantages of bio-oil are that it has a high energy density compared to raw biomass, while it is also easy to store, handle, and transport (Bridgwater et al., 1999; Meier and Faix, 1999; Bridgwater, 2012; Fonts et al., 2012; Wan Isahak et al., 2012; Huang et al., 2016). Bio-oil with an appropriate water content can be used directly as fuel in boilers, upgraded into fuel suitable for internal combustion engines, or turned into a high-value product for food and chemical processes (Bridgwater and Peacocke, 2000; Bridgwater, 2012; Wan Isahak et al., 2012). For the biochar and pyrolysis gas, they can be used as biofuels to generate heat or power for use in pyrolysis or other processes.

In spite of the above-mentioned advantages, the pyrolysis of biomass is still challenging due to the quantity and quality of the pyrolysis products being affected by many factors, including pyrolysis type, type of reactor, operating parameters, as well as biomass type and properties (Domínguez et al., 2006; Maddi et al., 2011; Pattiya, 2011; Pattiya and Suttibak, 2012a and b; Sirijanusorn et al., 2013; Kim et al., 2014; Odetoye et al., 2014; Kojima et al., 2015; Mao et al., 2015; Guda and Toghiani, 2016; Kurnia et al., 2016; Biswas et al., 2017; Guedes et al., 2018; Imran et al., 2018; Leng and Huang, 2018; Wang et al., 2018; Chen et al., 2019). For the oil palm biomass, it is well known that this type of biomass is non-woody and contains high levels of lignocelluloses. Most of the research works related to pyrolysis has used OPS, oil palm fiber, and EFB (Omar et al., 2011; Salema and Ani, 2011; Ruengvilairat et al., 2012; Abdullah et al., 2013; Asadullah et al., 2013; Sukiran et al., 2016; Kabir et al., 2017). However, the application of OPT and OPF biomass for the production of biofuels using pyrolysis processes is still a challenge as there are only a few studies that have investigated the pyrolysis of OPT and OPF (Yakub et al., 2015; Sareekam et al., 2016; Bensidhom et al., 2018), necessitating further studies to obtain in-depth insights into the process. In light of that, this study was aimed to investigate the yields and qualities of pyrolysis products obtained from OPT, OPF, and OPS using an agitated pyrolysis reactor. These three types of oil palm biomass were pyrolyzed under controlled operating conditions, and then the yield and quality of the pyrolysis products were determined and analyzed.

#### 2. Materials and Methods

#### 2.1. Preparation of oil palm biomass

The OPT and OPF used in this study were obtained from the oil palm trees, which had been harvested for 25 yr at Klong Thom District, Krabi Province, Thailand. The OPS was obtained from the Thiando palm oil factory (Lam Thap District, Krabi Province, Thailand). The fresh OPT (with bark) and OPF (without leaves) were processed through a chopping machine (MCH-420, Machinery789, Thailand). The chopped OPT and OPF were dried inside a solar greenhouse dryer to reduce the moisture content to below 10 wt.% (wet basis). The dried samples of OPT, OPF, and OPS were then further processed through a grinding machine (2 HP model, Bonny, Thailand), which was equipped with a 2 mm size sieve. The ground samples were kept in a sealed plastic bag for future use.

#### 2.2. Determination of physicochemical properties of oil palm biomass

## 2.2.1. Bulk density, proximate analysis, ultimate analysis, and heating value

The bulk density of the ground biomass samples was determined based on their mass and volume ratio using the modification method of Obernberger and Thek (2004). The moisture content, volatile matter, fixed carbon content, and ash content of the OPT, OPF, and OPS were determined by proximate analysis using a macro thermogravimetric analyzer (TGA 701, LECO, USA), according to the ASTM D7582 procedure. The elemental composition, including carbon (C), hydrogen (H), nitrogen (N), and sulphur (S), was determined by a CHNS/O Analyzer (FLASH 2000, Thermo Scientific, Italy), following the EN15104 and ASTM D4239 procedures. The oxygen (O) content was estimated by difference. The mean and standard deviation values were reported as percentages by weight (wt.%, dry basis). The higher heating value (HHV) of the biomass samples was determined by a bomb calorimeter (C5000, IKA<sup>®</sup> Werke, Germany), according to the EN14918 procedure.

#### 2.2.2. Lignocellulosic content

The lignocellulosic content of the OPT, OPF, and OPS was determined *via* the method developed by Georing and Van Soest (1970) and Van Soest (1991). According to this method, the percentages of cellulose, hemicellulose, and lignin were determined in terms of acid detergent fiber (ADF), neutral detergent fiber (NDF), and acid detergent lignin (ADL). The percentages (wt.%, dry basis) of cellulose, hemicellulose, lignin, and extractives were calculated by using the following equations (Eqs. 1, 2, 3, and 4):

| Cellulose content (CC)     | = | ADF-ADL      | Eq. 1 |
|----------------------------|---|--------------|-------|
| Hemicellulose content (HC) | = | NDF-ADF      | Eq. 2 |
| Lignin content (LC)        | = | ADL          | Eq. 3 |
| Extractives                | = | 100-CC-HC-LC | Eq. 4 |

#### 2.2.3. Thermogravimetric analysis (TGA)

The thermal decomposition behaviour of the oil palm biomass samples was observed *via* thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a thermogravimetric analyser (Perkin Elmer, USA), according to the ASTM E1131 procedure. The observation was performed at temperatures ranging from 50 to 1000°C and at a heating rate of 10°C/min under a nitrogen (N<sub>2</sub>) gas atmosphere.

#### 2.2.4. Major and minor elemental compositions

The major and minor elemental compositions, including silicon (Si), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), cadmium (Cd), and lead (Pb), of the biomass samples were determined *via* the Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES, AVIO500, Perkin Elmer, USA), according to the EN15297 procedure. The results were reported as mg/kg.

#### 2.3. Pyrolysis reactor setup

A schematic diagram of the agitated pyrolysis reactor used in this study is shown in **Figure 1**. The main components of the reactor include a reaction chamber, heating system with controller, electrical motor and agitated blade connected to a magnetic coupling drive and speed controller, cyclone, shell and tube condenser, water cooling bath, and nitrogen gas supplying system. The reaction chamber of the reactor was made from stainless steel (SUS316) with a diameter of 13 cm, a height of 15 cm, and a wall thickness of 5 mm. The reactor was equipped with a 3 kW electrical heater. The temperature of the biomass samples during the experiment was measured by a K-type thermocouple equipped with a stainless steel shield probe. The temperature of the biomass samples could be controlled by a PID-controlled system. The biomass sample inside the reaction chamber was mixed during the pyrolysis procedure by a mixing blade connected to an agitated motor via a magnetic coupling drive. The speed of the agitation motor was controlled by a speed controller. The N2 gas was supplied to the reactor through the bottom of the reactor. The flow rate of N2 gas could be controlled by a control valve, and its flow rate was measured by a flow meter. The vapor of the pyrolyzed biomass exited from the top of the reactor and flowed to the cyclone, which was used to remove solid particles from the pyrolysis vapor. The vapor was condensed in three series of shell and tube condensers, and the liquid product was collected in the collectors. Cold water was supplied to the condensers from a cooling water bath, which could control the water temperature in a range from 5-27°C. The flow rate of the cold water was measured by a rotameter equipped with a balancing valve. The incondensable gas could be recycled for use as a carrier gas with the control valve. The whole pyrolysis system was installed at the Prince of Songkla University, Hat Yai, Songkhla, Thailand.

#### 2.4. Experimental procedure

Before filling the biomass samples into the reaction chamber, the reaction chamber was heated to a temperature of  $97^{\circ}$ C. Then, 150 g of biomass sample was placed into the reactor chamber *via* the hopper and



Fig. 1. Schematic diagram of the pyrolysis reactor used in this study

control valve. The valve was then closed, and the reactor was heated continuously to the desired temperature. During the heating phase, the biomass was continuously mixed with a mixing blade at a speed of 10 rpm. When the temperature of the biomass was heated to 250°C, the N2 gas was purged through the reaction chamber at a flow rate of 2 L/min to maintain an inert atmosphere inside the reactor. During this period, the water used to supply the condenser was cooled by a cooling water bath to a temperature of 10°C. When the biomass temperature was increased to the set point temperature (400, 450 or 500°C), N<sub>2</sub> gas was supplied to the reaction chamber at a flow rate of 5 L/min. The vapor was immediately condensed in condensers with cold water at a temperature of 10°C and a flow rate of 8 L/min. The biomass was pyrolyzed for 30 min for each experiment. The condensable and incondensable vapors were considered as a liquid product and gaseous product, respectively. The solid residues remaining in the reaction chamber was considered as biochar. The yield of the liquid product and the biochar were directly determined by weighing. The yield of the pyrolysis gas was evaluated through a different method. The properties of the liquid product, biochar, and pyrolysis gas were determined and analyzed.

#### 2.5. Characteristics of the liquid product

#### 2.5.1. Water, solid, and ash content

The water content of the liquid product was determined by the volumetric Karl-Fischer titration technique using a Mettler Toledo V20 automatic titrator (Sirijannusom et al., 2013). The solids content of the liquid product was determined by the vacuum filtration technique. Briefly, the liquid product (3 g) was dissolved in 99.9% ethanol and filtered through a pre-dried Whatman No. 2 filter paper. The filter paper was then washed with ethanol until the filtrate was clear. The clear filter paper was dried with ambient air for 15 min and then dried in a hot air oven at 105 °C for 30 min. The dried paper was cooled in a desiccator before the mass was weighed (Pattiya and Suttibak, 2012a; Sirijannusom et al., 2013). The ash content of the liquid product was burned in a furnace at 775 °C with an oxygen supply for 24 h, following the procedure explained by Pattiya and Suttibak (2012a) and Sirijannusorn et al. (2013).

#### 2.5.2. pH value, density, ultimate analysis, and heating value

The pH value of the liquid product was measured by a pH meter (UB-10 Denver Instrument) at room temperature. Prior to measurement, the instrument was calibrated with standard liquid with a pH of 4, 7, and 10. The density of the liquid product was determined based on the weight and volume ratio using a density bottle at room temperature (Pattiya and Suttibak, 2012a; Sirijannusorn et al., 2013). The elemental composition of the liquid product was determined using the same method described in *Section 2.2.1*. The HHV of the liquid product was determined by a bomb calorimeter. Before determination, the liquid sample was dried in a hot air oven at 70°C until its weight was constant.

#### 2.5.3. Chemical compounds

The compounds of the liquid product were determined by using the gas chromatography-electron ionization/mass spectroscopy technique (GC-EI/MS) (Agilent CP9205, USA). The components of the liquid product were detected by FID, and the results were reported by comparing the peak areas of the sample and the standard. The capillary column was 30 m × 250  $\mu$ m × 0.25  $\mu$ m. The injection port and detector were operated at 250°C. The GC oven was heated to 70°C for 2 min, and then it was further heated to 250°C for 10 min at a heating rate of 5°C/min. The injection was performed with a 10  $\mu$ L liquid sample. The compounds were then identified using the National Institute of Standards and Technology (NIST) mass spectral library.

#### 2.6. Characteristics of biochar

#### 2.6.1. Proximate analysis, ultimate analysis, bulk density, and heating value

The proximate analysis, ultimate analysis and bulk density of the biochar were determined by using the same method, which was described in *Section* 2.2.1. The HHV of the biochar was calculated using the following correlation (Eq. 5) (Sheng et al., 2006):

HHV 
$$(MJ/kg) = Eq. 5$$
  
0 341C + 1 322H - 0 12O\* - 0 12N + 0 0686S - 0 0153Ash

where C, H, O\*, N, S, and Ash are percentages (on dry basis) of the carbon, hydrogen, oxygen, nitrogen, sulphur, and ash content of the biochar.

#### 2.6.2. Surface area

The surface area of the biochar was determined by BET (ASAP2460, Micromeritics, USA) using the static volumetric  $N_2$  gas adsorption method. The sample was pretreated under vacuum conditions at 80-200°C for 15 h. The adsorption-desorption isotherm was determined by the static volumetric method. The  $N_2$  gas was used as a carrier gas and an adsorbed gas. The pore volume was obtained by the adsorption isotherm with the multi condensation point (p/p0=0.05-0.03, 10-20 point) method. The pore structure was determined by the adsorption isotherm, and the average width was calculated by using the formula 4 V/A ("V" represents the pore volume while "A" denotes the adsorbed bet specific surface area).

#### 2.6.3. Surface morphology

Scanning electron microscopy (SEM) (JSM-5800 LV, JEOL, Japan) was used to observe the surface morphology of the biochar. The samples were coated with gold by sputtering before the SEM observations. The SEM was performed under high vacuum conditions with accelerating voltages of 20 kV and a secondary electron (SE2) detector with magnifications of 500-1000×.

#### 2.7. Pyrolysis gas composition and heating value

The composition of the pyrolysis gas was analyzed by a gas chromatograph (Micro GC, Agilent CP 4900) equipped with a thermal conductivity detectors (TCD). The channels were equipped with the MS5 and PPQ columns: Molsieve for separation of the  $H_2$ ,  $N_2$ , CO, and CH<sub>4</sub> at 80°C by helium used as the carrier gas. The HHV of the pyrolysis gas was estimated with the following equation (Eq. 6) (Suwannakuta, 2002):

| $HHV_{gas} (MJ/m^3) =$  | Eq. 6 |
|---|-------|
| $13.1(\% \text{CO}/100) + 13.2(\% \text{H}_2/100) + 41.2(\% \text{CH}_4/100)$ |       |

where CO,  $H_2$ , and  $CH_4$  are the percentages (by volume) of the carbon monoxide, hydrogen, and methane in the pyrolysis gas product.

#### 3. Results and Discussion

#### 3.1. Characteristics of oil palm biomass

#### 3.1.1. Proximate analysis and bulk density

Table 1 tabulates the proximate analysis, HHV, bulk density, elemental compositions, and lignocellulosic components of the OPT, OPF, and OPS. The proximate analysis showed that the moisture content, volatile matter, fixed carbon content, and ash content of the OPT, OPF, and OPS were in the ranges of 7.50-8.18, 66.59-74.06, 14.92-23.98, and 1.24-3.42 (wt.%), respectively. The moisture content of the dried biomass was lower than 10% (wt.), which is appropriate for pyrolysis processes (Bridgwater et al., 1999; Pattaya and Suttibak, 2012; Ahmad et al., 2017; Mishra and Mohanty, 2018). The moisture content of the biomass also strongly influences the water content in the obtained bio-oil or liquid product (Pattiya, 2011). Moreover, the high moisture content in the biomass necessitates extra heat to evaporate the moisture and increase the vapor temperature to the desired set point temperature, leading to high water content in the bio-oil or liquid product (Asadullah et al., 2008). For volatile matter, it can be seen that the volatile matter of the OPT and OPF were higher than in the OPS. The volatile matter of the OPT, OPF, and OPS was not much different from both woody and non-woody biomasses such as pine sawdust, sal sawdust, areca nut hush, rice straw, rice husk, date palm rachis, and date palm leaflets (Biswas et al., 2017; Kabir et al., 2017;

#### Table 1.

Physiochemical properties of the different types of oil palm biomass, i.e., oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS).

| Description of the second s | Types of oil palm biomass  |  |                                     |  |  |  |
|---|--|--|-------------------------------------|--|--|--|
| Properties and compositions   | OPT  | OPF  | OPS                                 |  |  |  |
| Proximate analysis  |  |  |                                     |  |  |  |
| Moisture content (wt.%, wet basis)  | $7.60\pm0.04$  | $7.50\pm0.04$  | $8.18 \pm 0.17$                     |  |  |  |
| Volatile matter (wt.%, dry basis )  | $74.06\pm0.60$   | $73.06\pm0.22$   | $66.59 \pm 0.21$                    |  |  |  |
| Fixed carbon (wt.%, dry basis)  | $14.92\pm0.51$   | $16.55\pm0.29$   | $23.98 \pm 0.15$                    |  |  |  |
| Ash content (wt.%, dry basis)   | $3.42\pm0.05$  | $2.89\pm0.05$  | $1.24\pm0.53$                       |  |  |  |
| Ultimate analysis (wt.%, dry basis)   |  |  |                                     |  |  |  |
| Carbon  | $43.68\pm2.14$   | $43.45\pm1.98$   | $50.72\pm3.12$                      |  |  |  |
| Nitrogen  | $0.40\pm0.02$  | $0.19 \ \pm 0.01$  | $0.33\pm0.03$                       |  |  |  |
| Hydrogen  | $6.07\pm0.26$  | $6.08 \pm 0.26$  | $6.00\pm0.40$                       |  |  |  |
| Oxygen <sup>*</sup>   | $49.85\pm2.40$   | $50.28 \pm 2.24$   | $49.92\pm3.56$                      |  |  |  |
| Sulphur   | < 0.01   | < 0.01   | < 0.03                              |  |  |  |
| Higher heating value (MJ/kg)<br>Bulk density (kg/m³)  | $\begin{array}{c} 16.11 \pm 0.23 \\ 151.83 \pm 2.96 \end{array}$ | $\begin{array}{c} 15.81 \pm 0.54 \\ 176.96 \pm 1.82 \end{array}$ | $18.72 \pm 0.36 \\ 702.61 \pm 3.33$ |  |  |  |
| Elemental compositions (mg/kg)  |  |  |                                     |  |  |  |
| Silicon (Si)  | 142.07   | 353.18   | 143.71                              |  |  |  |
| Iron (Fe)   | 1086.96  | 581.11   | 2438.06                             |  |  |  |
| Calcium (Ca)  | 1668.57  | 3817.1   | 21407.33                            |  |  |  |
| Magnesium (Mg)  | 10.98  | 1630.22  | 744.8                               |  |  |  |
| Sodium (Na)   | 431.83   | 209.15   | 47.87                               |  |  |  |
| Potassium (K)   | 175.63   | 20994.04   | 2708.62                             |  |  |  |
| Lignocellulosic content (wt.%, dry basis)   |  |  |                                     |  |  |  |
| Cellulose   | 39.40±0.77   | 54.35±0.29   | 37.95±0.28                          |  |  |  |
| Hemicellulose   | 25.97±1.17   | 20.72±0.12   | 11.52±0.01                          |  |  |  |
| Lignin  | 6.64±0.31  | 8.96±0.26  | 38.15±0.45                          |  |  |  |
| Extractives   | 27.99±0.41   | 15.96±0.53   | 12.38±0.41                          |  |  |  |

\* Calculated by difference

Bensidhom et al., 2018; Mishra and Mohanty, 2018). Volatile matter is an essential component of biomass for producing bio-oil or liquid product *via* pyrolysis processes. This is because the yield of bio-oil or liquid product depends on the volatile matter (Fonts et al., 2009; Pattiya, 2012). Based on the fixed carbon and ash content results, it can be seen that the OPS had a higher fixed carbon content compared to the OPT and OPF. The fixed carbon content

of the biomass cannot be converted into vapors or gases. However, this component can be converted into biochar. Thus, the pyrolysis of biomass to produce a high yield of biochar is appropriate with biomass that has a high fixed carbon content. The last component of the biomass is the ash content, which is an inorganic composition in the biomass. Biomass with a high ash content is not suitable for bio-oil production *via* pyrolysis processes because it leads to a low yield of bio-oil or liquid product while the amounts of biochar with inorganic elements will be high.

#### 3.1.2. Ultimate analysis and heating value

The C, N, H, S, and O contents of the OPT, OPF, and OPS, were in the ranges of 43.45-50.72, 0.19-0.33, 6.00-6.08, < 0.03, and 49.85-50.28 wt.%, respectively. The C and H contents of these biomasses were relatively high compared to the elemental composition of cassava rhizomes, cassava stalk, wheat straw, corn stalk, wood sawdust, corncob, and rice husk (Pattiya, 2011; Pattiya and Suttibak, 2012b; Biswas et al., 2017; Mishra and Mohanty, 2018). The results of the ultimate analysis are consistent with the proximate analysis results. The high fixed carbon content in the biomass led to a high C element as clearly observed in the cases of the OPS. The biomass with high C and H contents provided high HHV. The HHV of the biomass was also related to the volatile matter and fixed carbon content. The HHV of the OPT, OPF, and OPS was in the range of 15.81-18.72 MJ/kg. Separately, the HHV of the OPS was highest. The HHV of these biomasses was close to that of corn cob, wheat straw, rice straw, pine sawdust, oil palm fronds, oil palm mesocarp fiber, and date palm rachis (Biswas et al., 2017; Kabir et al., 2017; Bensidhom et al., 2018; Mishra and Mohanty, 2018). For the pyrolysis processes, the biomass with high C, high H, and low O content is favorable (Pimenidou and Dupont, 2012). This is because C and H can be converted into aromatics that are useful for making bio-oil or liquid product. On the other hand, the O will bond with the hydrocarbon molecules as oxygenated compounds, which reduce the effectiveness of biomass in terms of producing bio-oil. The pyrolysis of biomass with high O content also runs the risk of producing bio-oil or liquid product with high water content. This is because reaction water can be formed from the reaction between H and O (Pimenidou and Dupont, 2012). The N and S contents of the OPT, OPF, and OPS were low. The low amount of N and S in the biomass indicates that the formation of SO<sub>x</sub> and NO<sub>x</sub> is lower during the pyrolysis process (Mishra and Mohanty, 2018). The bulk density of the prepared biomass is directly related to the storage, handling, and transportation. In this study, the bulk densities of the OPT, OPF, and OPS was 151.83, 176.96, and 702.61 kg/m<sup>3</sup>, respectively. The bulk densities of the OPT and OPF were low compared to that of pine sawdust, sal sawdust, and areca nut husk (Mishra and Mohanty, 2018).

#### 3.1.3. Elemental composition

The major and minor elements of OPT, OPF, and OPS, are shown in Table 1. The investigated elements of the oil palm biomass samples included silicon (Si), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K). The contents of these elements were in the ranges of 142.07-353.18 mg/kg for Si, 581.11-2438.06 mg/kg for Fe, 1668.57-21407.33 mg/kg for Ca, 10.98-1630.22 mg/kg for Mg, 47.87-431.83 mg/kg for Na, and 175.63-20994.04 mg/kg for K. These results were consistent with those of Loh (2016). Previously, there have been many works which have revealed the alkali content of oil palm biomass, such as Na, Mg, K, and Ca, to be especially important in thermochemical conversion processes. This is because these elements may react with the Si at high temperature, resulting in operational problems with the reactors, furnaces, and boilers (Wei et al., 2005; Ninduangdee and Kuprianov, 2014; Sukiran et al., 2016). Alvarez et al. (2015) reported that the metals in the biomass resulted in catalytic activity on the pyrolysis products by promoting secondary reactions such as cracking and dehydration. These effects led to obtaining low bio-oil yields and high gas yields. Eom et al. (2012) concluded that some inorganic elements, such as Ca, Mg, and K, would promote the degradation of cellulose and hemicellulose from the biomass, favoring the formation of gas. Zhang et al. (2015) identified the synergetic effect of the co-pyrolysis of sewage sludge and rice husk. The high inorganic elements in sewage sludge led to a high gas yield of co-pyrolysis. Zuo et al. (2014) also found that the co-pyrolysis of poplar sawdust and sewage sludge in a

fixed bed reactor provided the maximum yield of bio-oil when they mixed 80% sludge with 20% sawdust.

#### 3.1.4. Lignocellulose content

The cellulose, hemicellulose, lignin, and extractives of the OPT, OPF, and OPS were in the ranges of 37.95-54.35, 11.52-25.97, 6.64-38.15, and 12.38-27.99 wt.%, respectively. The OPT and OPF contained high levels of cellulose and hemicellulose, while the OPS contained high levels of cellulose and lignin. The extractives were high in the OPT, which is consistent with its ash content. For the pyrolysis process, the biomass with the high levels of cellulose and hemicellulose content promoted higher yields of bio-oil or liquid product than the biomass with high lignin content. This is due to the fact that the thermal decomposition of lignin is more difficult than that of cellulose and hemicellulose. The pyrolysis of biomass with a high lignin content usually leads to a high biochar yield (Akhtar and Amin, 2012). Quan et al. (2016) studied the pyrolysis behavior of cellulose, hemicellulose, and lignin at 500°C and found that the pyrolysis of these components provided liquid yields of 18.67, 30.83, and 0.5% (wt.), respectively. Kim et al. (2013) found there was a higher bio-oil yield when using biomass with higher cellulose and hemicellulose contents. Qu et al. (2011) explained that the pyrolysis of cellulose provided a high bio-oil yield because cellulose is more volatile than hemicellulose. In addition to the liquid yield, variations in the composition of the cellulose, hemicellulose, and lignin in the biomass also influence the chemical compounds of the bio-oil or liquid product (Stefanidis et al., 2014; Chang et al., 2018).

#### 3.1.5. Thermal decomposition behavior

The TGA and differential thermogravimetric analysis (DTA) of the OPT, OPF, and OPS were performed to observe the thermal decomposition behavior as shown in Figures 2a and b, respectively. These figures clearly reveal that there were three main stages in the thermal decomposition due to the different components of the lignocellulose. The first stage occurred at temperatures of 50-120°C. At this stage, the weight of the biomass was decreased slightly due to the evaporation of the moisture content. In the second stage at temperatures of 120-250°C, the weight of the oil palm biomass was relatively constant due to the lower amount of evaporation of the light volatile compounds. Most of the thermal energy supplied to the biomass was used to increase biomass temperature during this stage. The next stage was the main thermal decomposition of the oil palm biomass, which occurred at temperatures of 250-500°C. During this stage, most of the volatile organics, including cellulose and hemicellulose, were decomposed as condensable and incondensable vapors or gases. For the last stage at temperatures above 500°C, the thermal degradation of the biomass samples was relatively slow due to the decomposition of the lignin. The thermal decomposition trends of oil palm biomass were consistent with the results on proximate analysis and lignocellulosic components. Previous research has found that the thermal decomposition of hemicellulose mainly takes place within the temperature range of 220-350°C, followed by cellulose decomposition, which primarily occurs at the temperature range of 325-400°C. Recent investigations have reported that lignin is the most stable component, decomposing in the higher temperature range of 300-900°C (Maddi et al., 2011; Kim et al., 2014; Stefanidis et al., 2014; Mishra et al., 2018; Chen et al., 2019).

#### 3.2. Pyrolysis products distribution

The product yields obtained from the pyrolysis of OPT, OPF, and OPS at temperatures of 400, 450, and 500°C are shown in Figures 3a, b, and c, respectively. It can be seen that the product yields of the liquid, biochar, and pyrolysis gas were in the ranges of 32.96-45.99, 23.41-37.51, and 25.23-37.58 wt.%, respectively. These results indicate that the different types of oil palm biomass and pyrolysis temperatures affected the product yields. The pyrolysis of the OPF provided a higher liquid yield than from OPT or OPS, while the pyrolysis of the OPS obtained the highest amount of biochar. The yields of the lignocellulosic components of the biomass. The pyrolysis of the biomass with a high volatile matter and a low ash content resulted in a high amount of liquid product. These results were similar with those of the previous studies, such as



Fig. 2. (a) Thermogravimetric analysis (TGA) and (b) differential thermal analysis (DTA) of different types of oil palm biomass, i.e., oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS).

Fonts et al. (2009), Pattiya (2012), and Dhyani and Bhaskar (2018), who reported that the pyrolysis of biomass with high levels of volatile matter provided high yields of bio-oil or liquid product. The results of the pyrolysis products also corresponded to the lignocellulose content of the biomass. As can be seen in Table 1, the OPF contained a high hemicellulose and cellulose content, while the lignin and extractives were low. Thus, the pyrolysis of the OPF provided the highest amount of liquid product. For the effect of the pyrolysis temperature on product yields, it can be seen that an increase in pyrolysis temperature had a small effect on the product yields obtained from the OPT and OPF. This is because most of the components of the OPT and OPF were cellulose and hemicellulose, and these components can completely decompose at temperatures below 500°C. However, an increase in the pyrolysis temperature for the OPS clearly affected the product yields, particularly the liquid product. This is due to OPS containing high levels of lignin, which can decompose at a wide range of temperatures (200-900°C). In the case of the biochar yield, it decreased with an increase in the pyrolysis temperature. The reduction of the biochar yield at higher temperatures was due to the greater primary decomposition of the biomass (Pattiva, 2011). This result corresponds to those of the previous studies on the pyrolysis of lignocellulosic biomasses. The effects of the cellulose, hemicellulose, and lignin content of the biomass on the



Fig. 3. Product yields of (a) oil palm trunk (OPT), (b) oil palm fronds (OPF), and (c) oil palm shell (OPS) at different pyrolysis temperatures.

yield of the pyrolysis products have been studied by many authors. Quan et al. (2016) studied the pyrolysis behavior of cellulose, hemicellulose, and lignin at 500°C and found that the pyrolysis of these components provided liquid yields of 18.67, 30.83, and 0.5 wt.%, respectively. The mentioned effects were also investigated by Kim et al. (2013), who found a higher bio-oil yield when using biomass with higher cellulose and hemicellulose contents. Qu et al. (2011) explained that the pyrolysis of cellulose provided a high bio-oil yield because cellulose is more volatile than hemicellulose.

#### 3.3. Characterization of liquid product

#### 3.3.1. Water content

The water contents of the liquid product samples ranging from 61.1-68.3 wt.% are presented in Figure 4. This result indicates that the different types of oil palm biomass and pyrolysis temperatures had a small effect on the water content of the liquid product. The results of the water content in the liquid products were consistent with those of the moisture contents, as well as the O and H contents in the oil palm biomass. Previous related studies reported that the initial moisture content of the biomass strongly influenced the water content in the obtained bio-oil or liquid product (Pattiya, 2011; Pattiya and Suttibak, 2012a and b). The water content of the bio-oil usually varies in the range of 10-40 wt.% (wet basis), depending on the biomass types and compositions as well as the pyrolysis conditions (Kang et al., 2006; Lu et al., 2009; Pattiya and Suttibak, 2012b; Odetoye et al., 2015; Guda and Toghiani, 2016). The pyrolysis of biomass with a high moisture content leads to obtaining bio-oil or liquid product with high water content. Thus, the moisture content in the biomass should be as low as possible in practice. However, the water content in bio-oil or liquid product not only depends on the moisture content of the biomass but is also influenced by the pyrolysis conditions, such as the heating rate, reactor types, vapor residence time, and pyrolysis temperature (Kang et al., 2006; Lu et al., 2009). Based on the results obtained from this study, it was observed that the water content of the liquid product samples was relatively high (>50 %) when compared to the values reported by the previous studies, such as Pattiya and Suttibak (2012a and b) and Sirijanusorn et al. (2013). This is because the pyrolysis reactor used in this study provided a low heating rate, which was about 14°C/min. When the pyrolysis of the biomass was performed at a slow rate, it was found that the water content of the bio-oil or liquid product was normally higher than 50 wt.%. Chen et al. (2011) reported that the water content of the bio-oil from the condenser was 64.41-75.09 wt.%. Moreover, the pyrolysis of biomass with a high O content runs the risk of obtaining bio-oil or a liquid product with high water content. This is because reaction water can be formed from the reaction between H and O (Pimenidou and Dupont, 2012). The higher water content in bio-oil leads to lower heating values, as well as the instability of the liquid product.

#### 3.3.2. pH, solid content, ash content, and density

Table 2 lists the properties of the liquid product samples in terms of pH, solid content, ash content, and density. The results show that the pH, solid content, ash content, and density of the liquid product samples were in the range of 2.67-3.0, 0.09-0.88 wt.%, 0.24-0.79 wt.%, and 919.73-1057.60 kg/m<sup>3</sup>, respectively. These results indicate that the different types of oil palm biomass and the pyrolysis temperature had small effects on the properties of the liquid product. The pH of the liquid product samples obtained from this work was in the general range for bio-oil or liquid product, which was 2.5-4 (Pattiya and Suttibak, 2012a and b; Sirijanusorn et al., 2013; Kabir et al., 2017). The liquid product samples had high pH values due to containing large amounts of acids, leading to a disadvantage for the bio-oil or liquid products in terms of direct applications. The solid content of the liquid product samples obtained from this work was relatively low compared to other types of moving bed pyrolysis reactors such as fluidized bed, twin screw, and free-fall reactors (Pattiya et al., 2012; Pattiya and Suttibak, 2012a; Sirijanusorn et al., 2013).

The solid content in the bio-oil and liquid product comes from the fine particles of the biomass and biochar. These solid particles could escape from the pyrolysis reactor if the reactor would be operated at a high nitrogen flow rate or if the pyrolysis reactor would be operated under high turbulence conditions, such as in the case of fluidized bed systems. Thus, the

#### Table 2.

Properties of liquid product obtained from pyrolysis of the different types of oil palm biomass, i.e., oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS).

| <b>D</b> . | <b>D</b>                     | Properties of liquid product |                      |                    |                              |  |  |
|------------|------------------------------|------------------------------|----------------------|--------------------|------------------------------|--|--|
| Diomass    | Pyrolysis temperature (°C) — | рН                           | Solid content (wt.%) | Ash content (wt.%) | Density (kg/m <sup>3</sup> ) |  |  |
|            | 400                          | $2.71\pm0.01$                | $0.09\pm0.02$        | $0.24\pm0.05$      | $1057.60 \pm 0.92$           |  |  |
| OPT        | 450                          | $2.74\pm0.01$                | $0.13\pm0.03$        | $0.24\pm0.02$      | $1050.87\pm0.42$             |  |  |
|            | 500                          | $2.91\pm0.01$                | $0.38\pm0.04$        | $0.47\pm0.07$      | $1045.33\pm0.61$             |  |  |
|            | 400                          | $2.95\pm0.01$                | $0.61\pm0.08$        | $0.74\pm0.02$      | $948.20\pm0.80$              |  |  |
| OPF        | 450                          | $2.77\pm0.01$                | $0.22\pm0.07$        | $0.40\pm0.03$      | $947.00\pm0.87$              |  |  |
|            | 500                          | $2.67\pm0.01$                | $0.37\pm0.07$        | $0.32\pm0.02$      | $932.20\pm0.40$              |  |  |
| OPS        | 400                          | $2.93 \pm 0.02$              | $0.88\pm0.08$        | $0.79 \pm 0.07$    | $940.07\pm0.95$              |  |  |
|            | 450                          | $2.71\pm0.01$                | $0.19\pm0.05$        | $0.38\pm0.02$      | $919.73\pm0.90$              |  |  |
|            | 500                          | $3.00\pm0.01$                | $0.32\pm0.07$        | $0.58\pm0.02$      | $926.73\pm0.40$              |  |  |



Fig. 4. Water content of liquid product of oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) at different pyrolysis temperatures.

installation of a cyclone, bag filter, and electrostatic precipitator (ESP) can help to reduce the solid content in the bio-oil or liquid product (Pattiya and Suttibak, 2012b; Sirijanusorn et al., 2013). The high solid content in the liquid product samples led to high ash contents after they were burned under oxidation conditions. This is because the solid particles in the liquid product samples were burned into ash, the inorganic component of the biomass. The ASTM burner fuel standard requires a liquid fuel with a solid content of lower than 0.25 wt.% (Oasmaa et al., 2009). For the density of the liquid product, it was

found that the density of the liquid product obtained from the OPT was relatively higher than for the OPF and OPS. Normally, the density of biooil with a low water content is about 1.0-1.1 g/mL (Pattiya and Suttibak, 2012a; Kabir et al., 2017). However, in the case of Fonts et al. (2009), they found that the density of their liquid product was lower than 1 g/mL.

#### 3.3.3. Ultimate analysis and HHV

The ultimate analysis results for the liquid product samples obtained from the OPT, OPF, and OPS at various pyrolysis temperatures are shown in Table 3. These results reveal that the C, N, H, O, and S contents of the liquid product were in the ranges of 11.92-22.20, 0.07-0.19, 2.97-6.32, 73.04-84.23, and 0.06-0.09 wt.%, respectively. Moreover, they indicate that the liquid product samples obtained from this study consisted mainly of oxygen-containing compounds and water. Oxygen in bio-oil or liquid product stems from the O in the cellulose, hemicellulose, and lignin fractions of the biomass (Pattiva and Suttibak, 2012a). Pattiva and Suttibak (2012a) also reported that the elemental compositions of bio-oil might be related to its solids and water contents. The hydrocarbon content of the liquid product was only 15-27 wt.%, which was similar to the results of Alvarez et al. (2015). Based on the obtained results, it was observed that an increase in the pyrolysis temperature led to the lower C content in the liquid product. This is because the non-condensable vapor was higher when there was an increase in the pyrolysis temperature. However, the liquid product samples contained low amounts of N and S since the biomass used in this study had low N and S contents. The hydrocarbon content of bio-oil with low water contents can range from 60-80 wt.% (Pattiya and Suttibak, 2012b; Kabir et al., 2017; Bensidhom et al., 2018). For the HHV of the liquid product, this study determined the HHV of water-free liquid product. The results showed that the HHV scores of the samples were in the range of 18.95-22.52 MJ/kg, as shown in Figure 5. These HHVs were relatively low when compared to the studies of Pattiya and Suttibak (2012b) and Sirijanusorn et al. (2013), who performed the pyrolysis of cassava biomass with a fast pyrolysis reactor. Kabir et al. (2017) and Bensidhom et al. (2018) also found that the HHV of bio-oil was 21-25 MJ/kg.

#### 3.3.4. Compounds of liquid product

Table 4 presents the compounds of the liquid product obtained from the OPT, OPF, and OPS at a pyrolysis temperature of 500°C. The results indicated that the main compounds of the liquid product samples were

 Table 3.

 Ultimate analysis of liquid product obtained from pyrolysis of the different types of oil palm biomass, i.e., oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS).

| Biomass | Purolucis topporture (°C) | Ultimate analysis results of liquid product (% wt.) |                 |           |            |                 |
|---------|---------------------------|---|-----------------|-----------|------------|-----------------|
|         | Tyrorysis temperature (C) | Carbon  | Nitrogen        | Hydrogen  | Oxygen*    | Sulphur         |
|         | 400                       | 16.16±0.73  | 0.19±0.02       | 2.97±0.18 | 80.63±0.57 | 0.07±0.00       |
| OPT     | 450                       | 13.98±0.11  | $0.17 \pm 0.02$ | 5.97±0.35 | 79.82±0.44 | $0.08 \pm 0.01$ |
|         | 500                       | 11.92±0.21  | $0.11 \pm 0.00$ | 3.69±0.25 | 84.23±0.46 | 0.07±0.01       |
|         | 400                       | 13.74±1.00  | $0.11 \pm 0.01$ | 5.22±0.54 | 80.88±1.56 | 0.07±0.01       |
| OPF     | 450                       | 13.49±0.49  | $0.09 \pm 0.00$ | 3.58±0.21 | 82.79±0.71 | 0.06±0.01       |
|         | 500                       | 12.53±0.40  | 0.07±0.00       | 3.57±0.43 | 83.79±0.84 | 0.06±0.01       |
|         | 400                       | 22.20±0.05  | $0.19 \pm 0.01$ | 4.52±0.53 | 73.04±0.48 | 0.07±0.01       |
| OPS     | 450                       | 17.97±1.16  | 0.15±0.00       | 6.32±0.40 | 75.48±0.76 | $0.09 \pm 0.00$ |
|         | 500                       | 17.74±1.24  | $0.15 \pm 0.00$ | 5.18±0.20 | 76.86±1.04 | $0.08 \pm 0.01$ |

\* calculated by difference

Compounds of liquid product obtained from pyrolysis of the different types of oil palm biomass, i.e., oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) at the temperature of 500°C.

|     |  |                                 | Peak area (%) |       |       |
|-----|--|---------------------------------|---------------|-------|-------|
| No. | Compounds                              | Formula                         | OPT           | OPF   | OPS   |
| 1   | Furan,2,5-diethoxytetrahydro-          | $C_8H_{16}O_3$                  | 0.17          | 0.22  | 0.24  |
| 2   | Furan,2-ethyl-                         | $C_6H_8O$                       | 0.07          | 0.05  | 0.04  |
| 3   | Acetic Acid                            | $C_2H_4O_2$                     | 13.39         | 10.32 | 14.49 |
| 4   | 2-Furan-carboxaldehyde                 | $C_5H_4O_2$                     | 4.41          | 6.63  | 3.34  |
| 5   | 2-Furanethanol                         | $C_5H_6O_2$                     | -             | -     | 1.78  |
| 6   | 3-Furanethanol                         | $C_5H_6O_2$                     | 2.93          | 1.23  | -     |
| 7   | Phenol                                 | C <sub>6</sub> H <sub>6</sub> O | 9.32          | 8.17  | 3.32  |
| 8   | Phenol,2-methoxy-                      | $C_7H_8O_2$                     | 1.65          | 2.23  | 2.78  |
| 9   | Phenol,2,6-demethoxy-                  | $C_8H_{10}O_3$                  | 2.96          | 0.11  | 3.85  |
| 10  | Phenol,2,6-demethoxy-4-(2-propenyl)-   | $C_{11}H_{14}O_3$               | 0.15          | 0.13  | 0.28  |
| 11  | 2-Propanone,1-hydroxy-                 | $C_3H_6O_2$                     | 6.69          | 5.36  | 4.65  |
| 12  | 4-proyl-syringol                       | $C_{11}H_{16}O_3$               | 0.10          | 0.10  | 0.15  |
| 13  | 2-Cyclopenten-1-one,3-ethyl-2-hydroxy- | $C_7H_{10}O_2$                  | 0.61          | 0.52  | 0.35  |
| 14  | Octanoic acid                          | $C_8H_{16}O_2$                  | -             | -     | 0.33  |
| 15  | Benzenemethanol                        | C7H8O                           | -             | 0.63  | 0.43  |
| 16  | 3,5-Dimethoxy-4-hydroxytoluene         | $C_9H_{12}O_3$                  | 1.01          | 1.18  | 1.88  |
| 17  | Benzene, 123-trimethoxy-5-methyl-      | $C_{10}H_{14}O_3$               | -             | 0.54  | -     |
| 18  | Benzaldehyde,4-hydroxy-3-methoxy-      | $C_8H_8O_3$                     | 0.10          | 0.29  | 0.42  |
| 19  | 2-Methoxy-4-vinylphenol                | $C_9H_{10}O_2$                  | 0.21          | -     | 0.46  |
| 20  | 2,6-Dimethoxy-4-(prop-1-en-1yl)phenol  | $C_{11}H_{14}O_3$               | 0.08          | 0.06  | 0.15  |



Fig. 5. Higher heating value (HHV) of liquid product of oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) at different pyrolysis temperatures.

Table 5.

Proximate analysis results and bulk density of biochar.

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such as furan and furan derivatives and acetic acid. The lignin fraction of the biomass was devolatilized to pervade the resulting liquid product with oxygenated aromatic compounds such as phenols and phenolic derivatives (Chen et al., 2016; Li et al., 2017; Kabir et al., 2017). Beside the lignin content, the alkali metals of the biomass also influenced the compounds of the liquid product. Kabir et al. (2017) explained that the contact of alkali metals with the pyrolysis vapor catalyzed the conversion of the levoglucosan to light organic compounds such as acetic acid and furfural. The amounts of acid compounds in the obtained liquid product indicated that the pyrolysis product was highly acidic, which was consistent with the pH of 2.67-3, as shown in Table 2. Bio-oil or liquid product with low pH values are not appropriate for direct use because they encourage aging and corrosivity (Kabir and Hameed, 2016).

#### 3.4. Characteristics of biochar

#### 3.4.1. Proximate analysis, ultimate analysis, HHV, and bulk density

**Tables 5** and 6 show the results on proximate analysis, bulk density, and ultimate analysis of the biochar obtained from OPT, OPF, and OPS at various pyrolysis temperatures. The results indicated that the moisture content, volatile matter, fixed carbon content, and ash content of the biochar were in the range of 2.40-4.34, 12.09-24.39, 56.34-73.03 and 9.22-16.87 wt.%, respectively. Differences in the type of oil palm biomass and pyrolysis temperature affected the composition of the biochar. The gross composition of the biochar as indicated by proximate analysis corresponded to the composition of raw oil palm biomass. It was observed that the moisture content of biochar was not zero after pyrolyzing at temperatures ranging from 400 to 500°C. This result was consistent with those of the study conducted by Kabir et al. (2017), where biochar contained 3.06-4.42% moisture content. The volatile matter of the biochar remained

| Biomass | Pyrolysis        | Compositions of biochar (% wt.) |                 |              |             |                                     |
|---------|------------------|---------------------------------|-----------------|--------------|-------------|-------------------------------------|
|         | temperature (°C) | Moisture content                | Volatile matter | Fixed carbon | Ash content | - Bulk density (kg/m <sup>2</sup> ) |
|         | 400              | 4.02±0.04                       | 18.09±0.30      | 65.99±0.24   | 11.90±0.13  | $100.33\pm0.42$                     |
| OPT     | 450              | 3.15±0.08                       | 15.53±0.15      | 68.81±0.35   | 12.51±0.18  | $100.29\pm0.36$                     |
|         | 500              | 3.68±0.05                       | 12.09±0.36      | 71.83±0.30   | 12.41±0.17  | $93.69 \ \pm 0.82$                  |
|         | 400              | 4.34±0.02                       | 16.30±0.38      | 70.12±0.45   | 9.22±0.13   | $133.24\pm0.36$                     |
| OPF     | 450              | 3.64±0.01                       | 14.70±0.26      | 71.90±0.37   | 9.77±0.28   | $132.71\pm0.42$                     |
|         | 500              | 3.15±0.02                       | 13.59±0.19      | 73.03±0.58   | 10.22±0.42  | $123.93\pm0.24$                     |
| OPS     | 400              | 2.40±0.31                       | 24.39±0.26      | 56.34±0.56   | 16.87±0.68  | $563.16\pm2.12$                     |
|         | 450              | 2.89±0.16                       | 22.59±0.24      | 58.77±0.41   | 15.75±0.68  | $558.77\pm2.01$                     |
|         | 500              | 2.40±0.08                       | 17.11±0.64      | 66.93±1.68   | 13.56±1.01  | $484.27\pm1.83$                     |

oxygenated compounds such as acetic acid, furans, phenols, and 2-Propanone,1-hydroxy-. The high content of these compounds is responsible for the low HHV of the liquid product, which was consistent with the results shown in **Figure 4**. The concentration of each compound in the liquid product depended on the type of oil palm biomass and its composition, particularly the lignocellulosic components. Previous studies have revealed that biomass compositions strongly influence the compounds in bio-oil or liquid product (Maddi et al., 2011; Odetoye et al., 2014; Kojima et al., 2015; Kabir et al., 2017; Wang et al., 2018). The cellulose and hemicellulose in the biomass were decomposed to glucopyranoses (anhydrosugars) and heterocyclic compounds between 12.09-24.39 wt.%, indicating the incomplete pyrolysis of the OPT, OPF, and OPS under the investigated temperatures. More specifically, the volatile matter of the biochar was relatively high, particularly the biochar from the OPS. This could be ascribed to the high lignin levels of OPS, decomposing at high temperatures. An increase in the pyrolysis temperature clearly influenced the lower levels of volatile matter and higher levels of fixed carbon content. This is due to the fact that an increase in the pyrolysis temperature could contribute to the greater decomposition of the lignocellulosic components. The biochar of the OPT, OPF, and OPS

#### Table 6.

Ultimate analysis results of biochar.

| Biomass |                              | Elemental compositions of biochar (% wt.) |                 |           |            |                 |  |
|---------|------------------------------|---|-----------------|-----------|------------|-----------------|--|
|         | Pyrolysis temperature (°C) — | Carbon                                    | Nitrogen        | Hydrogen  | Oxygen*    | Sulphur         |  |
|         | 400                          | 71.09±0.15                                | 0.97±0.04       | 2.92±0.04 | 24.96±0.10 | 0.07±0.00       |  |
| OPT     | 450                          | 72.88±0.26                                | 0.94±0.00       | 2.53±0.08 | 23.58±0.19 | $0.08 \pm 0.00$ |  |
|         | 500                          | 75.28±0.02                                | 0.70±0.01       | 2.30±0.02 | 21.67±0.30 | $0.05 \pm 0.00$ |  |
|         | 400                          | 73.97±0.07                                | 0.41±0.01       | 2.59±0.09 | 22.87±0.07 | 0.15±0.01       |  |
| OPF     | 450                          | 75.65±0.84                                | $0.40 \pm 0.01$ | 2.62±0.02 | 21.26±0.87 | 0.06±0.00       |  |
|         | 500                          | 75.71±0.31                                | 0.39±0.00       | 2.42±0.02 | 21.42±0.34 | 0.06±0.00       |  |
| OPS     | 400                          | 60.18±0.20                                | 0.61±0.01       | 2.56±0.00 | 36.55±0.20 | 0.11±0.01       |  |
|         | 450                          | 74.08±0.34                                | 0.63±0.01       | 2.95±0.06 | 22.33±0.41 | 0.02±0.00       |  |
|         | 500                          | 77.15±0.10                                | 0.61±0.00       | 2.65±0.04 | 19.58±0.06 | 0.01±0.00       |  |

\* Calculated by difference



Fig. 6. Higher heating value (HHV) of biochar of oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) at different pyrolysis temperatures.

contained a high ash content when compared to the raw biomass. The high ash content in the biochar was due to the high levels of alkali metals in the biomass, as mentioned earlier.

The results of the proximate analysis were consistent with the ultimate analysis results. **Table 6** shows the elemental compositions of the biochar. It is seen that the C, N, O, and S contents of the biochar were in the ranges of 60.18-77.15, 0.39-0.97, 19.58-36.55, 2.30-2.95, and 0.01-0.15 wt.%, respectively. For the OPT and OPF, an increase in the pyrolysis temperature had a small effect



Fig. 7. Bulk density of biochar of oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) at different pyrolysis temperatures.

on the elemental composition of the biochar. However, for the OPS, the C and O contents were evidently lower at higher pyrolysis temperatures. These results clearly showed that the pyrolysis of biomass produced biochar with a high C content and a low O content, which is similar to the findings of the previous studies (Maddi et al., 2011; Alvarez et al., 2015; Bensidhom et al., 2018). The higher C content and lower O content of the biochar led to superior HHV. The HHV of the biochar obtained from the OPT, OPF, and OPS at different pyrolysis temperatures is shown in Figure 6. It is seen that the HHV of the biochar was between 25.14 and 28.45 MJ/kg. This is relatively consistent with its elemental co mposition. Generally, the HHV of biochar obtained from biomass pyrolysis using slow and fast pyrolysis

reactors ranging from 20-32 MJ/kg is dependent on the type of biomass used and the pyrolysis conditions (Maddi et al., 2011; Pattiya and Suttibak, 2012b; Kabir et al., 2017; Bensidhom et al., 2018). Although the HHV of the biochar was higher than that of the raw biomass, the bulk density of the biochar was low, as shown in **Figure 7**. This indicates that the biochar of the OPT and OPF had a very low bulk density ranging from 93.69 to 133.24 kg/m<sup>3</sup>. The biochar of the OPS had a relatively high bulk density when compared to the biochar of the OPT and OPF. Biochar with a low bulk density is not appropriate for storage and transportation. Thus, processing the biochar into pellets and briquettes to increase its bulk density and energy density can help to overcome the limitations of biochar for fuel applications.

**Figures 8a-f** show the surface features of the biomass and biochar obtained from OPT, OPF, and OPS at a pyrolysis temperature of 500°C. These images clearly show the porous structures of the biochar, particularly the biochar from the OPT and OPF. The morphology of OPT and OPF biochar revealed pores created over the surface, with the size and shape of the pores clearly seen. The pores are arranged in an orderly fashion with a pore size of about 2  $\mu$ m. The shape of the pores at the surface appears like a honeycomb with cylindrical and polygonal pores. This is similar to the findings of Bensidhom et al. (2018). In the case of OPS biochar, the pore



Fig. 8. SEM images of a) oil palm trunk (OPT), b) biochar of OPT, c) oil palm fronds (OPF), d) biochar of OPF, e) oil palm shell (OPS), and f) biochar of OPS at the pyrolysis temperature of 500 °C.



Fig. 9. Surface area of biochar of oil palm trunk (OPT), oil palm fronds (OPF), and oil palm shell (OPS) at the pyrolysis temperature of 500°C.

size and shape were not clear at a magnification of 1000×. This is because the OPS contained high levels of lignin, giving OPS a hard and dense solid structure (high density). Consequently, the pyrolysis of the OPS at 500°C did not completely devolatilize most of the lignin, and the pores were not fully developed (Claoston et al., 2014). However, the BET analysis of the biochar found that the surface area of the OPS biochar was higher than of those of the OPT and OPF biochar, as shown in **Figure 9**. It is seen that the surface area of the OPT, OPF, and OPS biochar was 1.50, 2.27, and 4.4 m<sup>2</sup>/g, respectively. The high porous structure of these types of biochar mark them as alternatives for further application likes production of activated carbon.

#### 3.5. Pyrolysis gas composition and heating value

Table 7 shows the main composition and heating value of the pyrolysis gas product. It was found that pyrolysis gas product obtained from this study

#### Table 7.

Composition and heating value of pyrolysis gas.

contained low concentrations of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. The concentrations of these gases were in the ranges of 0-6.5, 0.34-14.17, 0.32-3.11, and 0.33-3.97 v/v%, respectively. The low concentration of each pyrolysis gas in this study was due to using a slow pyrolysis process and batch experiment. The N<sub>2</sub> flow rate supplied to the reactor was also relatively high. The slow heating rate and high N2 flow rate influenced the pyrolysis gas composition. For the effect of oil palm biomass types and pyrolysis temperatures, the results indicated that the type of oil palm biomass and the pyrolysis temperature affected the concentrations of the pyrolysis gases. The pyrolysis gas from the OPT contained higher concentrations of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> than the products obtained from the OPF and OPS. This is because the OPT contained high levels of cellulose and hemicellulose, while its lignin content was low. Cellulose and hemicellulose can decompose and be released as vapor at lower temperatures compared to lignin. The OPS contained high levels of lignin; therefore, the obtained pyrolysis gas was composed of very low concentrations of each gas. When the temperature of the pyrolysis increased, the concentration of each pyrolysis gas decreased. The lower concentration of each gas was due to the decomposition of light volatiles before reaching the set point temperature. The low concentrations of CO, H<sub>2</sub>, and CH<sub>4</sub> in the pyrolysis gas resulted in a low HHV of between 0.19 and 2.90 MJ/kg. When compared to the concentrations of pyrolysis gas products obtained from previous studies (Dominguez et al., 2006; Fonts et al., 2009; Pattaya, 2011; Alvarez et al., 2015; Mao et al., 2015; Bensidhom et al., 2018), there is a clear difference between their results and the results of the present study. The composition and concentration of the pyrolysis gas depend on many factors, such as the reactor type, biomass type and composition, heating rate and heating method, pyrolysis temperature, and N<sub>2</sub> flow rate. Thus, based on the obtained results, it can be concluded that the pyrolysis gas product has a low potential for gas fuel applications.

#### 4. Conclusions

This study investigated the yields and qualities of pyrolysis products obtained from OPT, OPF, and OPS using an agitated pyrolysis reactor. The oil palm biomass was pyrolyzed at pyrolysis temperatures of 400, 450, and 500°C. Then, the yield and quality of pyrolysis products, including liquid product, biochar, and pyrolysis gas were determined and analyzed. The results showed that the yields and qualities of pyrolysis products were dependent on the type of oil palm biomass used and the pyrolysis temperature. The pyrolysis of OPF at 500°C obtained the highest liquid yield. The pyrolysis of OPS provided the highest amount of biochar. The obtained liquid product contained high water content with low pH, resulting in highly-oxygenated compounds as indicated by GC-EI/MS. The HHV of the liquid product was low (18.95-22.52 MJ/kg) while the HHV of the biochar was relatively high (25.14-28.45 MJ/kg). The biochar can be considered as an alternative for activated carbon or bio-filter applications as indicated by SEM and BET. The obtained pyrolysis gas had a low potential for fuel applications.

| Biomass | Pyrolysis        |                |      |                 |                 |               |
|---------|------------------|----------------|------|-----------------|-----------------|---------------|
|         | Temperature (°C) | $\mathbf{H}_2$ | СО   | CH <sub>4</sub> | CO <sub>2</sub> | - HHV (MJ/NM) |
|         | 400              | 3.11           | 6.5  | 3.97            | 14.17           | 2.90          |
| OPT     | 450              | 1.38           | 2.99 | 1.95            | 6.04            | 1.38          |
|         | 500              | 0.93           | 1.02 | 1.32            | 1.68            | 0.80          |
|         | 400              | 0.85           | 3.99 | 2.1             | 9.15            | 1.50          |
| OPF     | 450              | 0.36           | 0.38 | 0.79            | 0.72            | 0.42          |
|         | 500              | 0.76           | 0.34 | 0.92            | 0.57            | 0.52          |
| OPS     | 400              | 0.19           | 1.73 | 1.9             | 2.96            | 1.03          |
|         | 450              | 0.32           | 0.78 | 1               | 0.86            | 0.56          |
|         | 500              | 0.38           | 0.00 | 0.33            | 0.34            | 0.19          |

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