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Upgrading of Bio-oil from Energy Crops via Fast Pyrolysis using Nanocatalyst in a Bubbling Fluidized Bed Reactor

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ABSTRACT

The aim of this research is to evaluate the catalytic efficiency of TiO_2 nanocatalyst in fast pyrolysis. Leucaena leucocephala was used as the feedstock pyrolyzed in the presence of TiO_2 catalyst in a bubbling fluidized bed reactor. The influence of pyrolysis temperature, catalytic zone temperature and TiO_2 catalyst to biomass (T/W) ratio on bio-oil production was evaluated. The structure and surface chemistry of TiO_2 catalyst were characterized by various analytical techniques. The characteristics and composition of the biomass were also investigated. In the absence of the catalyst, the maximum bio-oil yield of 54.21% was achieved at a pyrolysis temperature of 500°C. Regarding the influence of catalytic zone temperature, pyrolysis at 600°C using the T/W ratio of 1:1 resulted in an upgraded bio-oil product the yield of which was 59.98%. The obtained bio-oil contained 27.1% oxygen content with the HHV of 29.1 MJ/kg, indicating the TiO_2 catalyst could enhance the yield of bio-oil, accompanied by a decrease in gas generation. Moreover, in this study, the maximum yield 67.1% was obtained using 3:1 T/W ratio. The obtained bio-oil consisted of oxygen content 24.5% and generated the highest HHV of 31.5 MJ/kg. Thus, the TiO_2 catalyst had a potential for improving production efficiency of bio-oil product.

1. INTRODUCTION

Although fossil fuels such as coal, oil and natural gas are associated to the levels of development of a country, there is an increasing concern with the environment problems resulting from fossil fuels combustion [1]. It leads to large amounts of carbon dioxide (CO_2) emissions into the atmosphere. CO_2 is a primary greenhouse gas which is responsible for global warming and climate change [2]. In addition, world oil and gas reserves are being depleted, coupled with rapidly growing consumption rate resulting in a rise in crude oil price. Therefore, several studies were investigated to find the alternative fuels for sustainable development such as biofuels, electric fuel, and hydrogen fuel. In particular, biofuels (bio-oil, bioethanol and biodiesel) have the potential to be an alternative to petroleum products and their derivatives since bio-oil is considered to be a very promising resource. Bio-oil is well known as a renewable, sustainable, non-toxic, biodegradable, and eco-friendly alternative that can be substituted for conventional petroleum oils perfectly and that is a liquid fuel produced from lignocellulosic biomass through fast pyrolysis. The use of biomass can greatly reduce the nation's greenhouse gas emissions [3] and so does directly contribute to the mitigation of the global warming problem.

Fast pyrolysis has been considered as an attractive process for the transformation of biomass into alternative liquid fuels involving the thermochemical conversion occurring in the absence of oxygen. Biomass decomposes very quickly under a very high heating rate of the particles, very short hot vapour residence time (less than 2 s), and high reaction temperature between 450 and 1000°C to generate the high heating value liquid product (bio-oil), gases, and the solid residue (char). The main product is bio-oil in yields of 60-70% by mass [4], [5]. The composition and yield of the pyrolysis product largely depend on the source of biomass and process parameters [6]. However, in previous studies, liquid bio-oil from fast pyrolysis exhibited a wide range of molecular weight and boiling point. The complex mixture is a low-grade liquid fuel containing many undesirable compounds including water, acids, aldeydes phenolics, furans, and large molecular oligomers relate to undesired properties such as high oxygen and water content [7]. The substantial high oxygen content and the poor chemical stability make bio-oil significantly differ from the petroleum fuels [8]. For this reason, several methods were presented to upgrade the bio-oil to improve its properties, which required a decrease of the O/C ratio

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and an increase in the H/C ratio. The reaction mechanism is involved with the elimination of the oxygenated molecules which can be performed through three main pathways: decarboxylation, decarbonylation and dehydration. Usage of catalytic pyrolysis technology is the best method to eliminate the oxygenated compounds to upgrade bio-oil to advanced biofuels. It can be incorporated by directly adding the solid catalyst into a fast pyrolysis system (mixed with biomass feedstock) or by using a catalyst reactor coupled in the secondary reactor where they are catalytical upgraded [9]. In the reported literatures, a variety of catalysts were described for biomass catalytic pyrolysis such as zeolites, noble transition metals, clays, metal oxides, and metal salts [4], [9], [10]. The application of zeolitic catalysts has attracted considerable attention to upgrade bio-oil by increasing aromatic hydrocarbons and decreasing the oxygen content because of the bifunctional shape selectivity to obtain product in the range of fossil fuel properties. However, zeolites cause reduction of the bio-oil yield as it promotes the secondary cracking, whereas the catalyst suffers from rapid deactivation due to coke formation.

Therefore, seeking a viable alternative catalyst was considered to increase the bio-oil yield and upgrade the bio-oil quality. The present study aims to evaluate the catalytic activity of TiO_2 nanocatalyst in the thermochemical process of biomass pyrolysis of bio-oil production. *Leucaena leucocephala* was used as the biomass feedstock for bio-oil production. *Leucaena leucocephala* was chosen because it is an energetic crop with the fastest growth rate of woody mass which is superior for its holocellulose value resulting in a higher heating value [11]. The experiments were carried out in a bubbling fluidized bed reactor at a constant temperature under oxygen-free conditions. The bubbling fluidized bed reactor was applied for fast pyrolysis due to good control of the process and high energy density in bed with high heat transfer [12]. This research evaluated the influence of three key parameters; temperature of the pyrolysis zone; temperature of the catalytic zone and the TiO_2 catalyst to wood ratio (T/W ratio). Therefore, the effect of temperature and the catalyst dosage on the product yields, oxygen content and the HHV value was investigated. Comparative studies on efficiency of the catalyst in bio-oil production were conducted through the pyrolysis of *Leucaena leucocephala.* Moreover, the structure and surface chemistry of TiO_2 catalyst were characterized by various analytical techniques.

2. EXPERIMENTS

2.1 Biomass Feedstock and Characterization

The dried biomass obtained from *Leucaena leucocephala* was employed as the feedstock consisting of cellulose (48%) and hemicellulose (20%) for the catalytic fast pyrolysis experiment. This material was collected from sawmill, Thailand. It was shredded into coarse particles. Afterwards, it was ground and sieved by sieve shakers to achieve the desired particle size of <1.0 mm and then the air was dried. The proximate analysis of biomass was evaluated to determine moisture content, volatile matters, fixed carbon, and ash. The ultimate analysis was performed to determine elemental compositions of carbon, hydrogen, nitrogen, and sulfur content, while the oxygen content was estimated by calculation from the percentage difference. The higher heating value (HHV), bulk density and particle density were also investigated.

2.2 Catalyst and Characterization

The catalyst employed in this work was a commercial TiO_2 powder, type P25 (ca. 80% anatase, 20% rutile) with nanocrystalline features. The surface area and pore diameter were measured using the Brunauer-Emmet-Teller (BET) under a flow rate of nitrogen. SEM micrographs were performed using Quanta 200 scanning electron microscope to investigate the morphology. The X-ray diffraction (XRD) patterns were obtained with an Empyrean diffractometer, PANalytical, Netherlands to study the crystal structure. IR spectra were recorded on the sample/KBr mixture pallets using a Vertex70 FT-IR spectrophotometer (Bruker) to identify chemical bonds in the catalyst structure. The chemical composition of catalyst was estimated by Energy-dispersive X-ray spectroscopy (EDX). Particle size distribution was obtained using Imagej analysis and visualized in OriginPro 2021 (OriginLab Corporation, 2021).

2.3 Catalytic Activity Test of TiO_2 for Bio-oil Production

The biomass was pyrolyzed in the bubbling fluidized bed reactor. Details and schematic diagram of this experiment setup are shown in Figure 1. The major components of system were pre-heater, biomass tank, biomass feeding system, fluidized bed reactor, cyclone, hot filter, catalytic reactor, vapour condenser, electrostatic precipitator, and dry ice condenser. Approximately 100 g of biomass was placed in the biomass tank and then fed into the reactor by screw feeder at a rate of 1.6 g/min with a nitrogen flow rate of 3 L/min. The reactor system was operated under N_2 atmosphere at a total N_2 flow rate of 11 L/min to ensure that the system was under an inert atmosphere in which N_2 was fed through the bottom of the fluidized reactor under the gas flow rate of 7 L/min. Silica sand was used as the bed in the fluidized bed reactor with size of 0.2-0.5 mm. The reactor was divided into two separated zones. The pyrolysis zone is the non-catalytic section that was operate under a heating rate of 15°C/min at different temperature (400, 450, 500, 550, and 600°C). The fluidized bed reactor was made of stainless steel 304 with internal diameter of 50 mm and height of 450 mm. The reactor was heated by electric resistance wire to maintain the pyrolysis temperature. The catalytic zone was heated by two independent electrical furnaces. The effect catalytic zone temperature was also investigated over the temperature. The catalyst was placed in the catalytic zone. The catalytic performance of the TiO_2 catalyst was investigated varying the TiO_2 catalyst to wood ratio (T/W) in the range of 1:1-3:1. The pyrolysis vapour was then condensed in the water-cooled condenser and ice bath connected in series. Liquid product was finally collected in a bottle for their further analysis. Char was produced in the pyrolysis zone, thus avoiding contact of the catalyst. Char was then separated in the cyclone separators. Afterward, char was collected for their further study. The efficiency of TiO_2 catalyst was evaluated in terms of the mass yield, oxygen content and bio-oil properties.

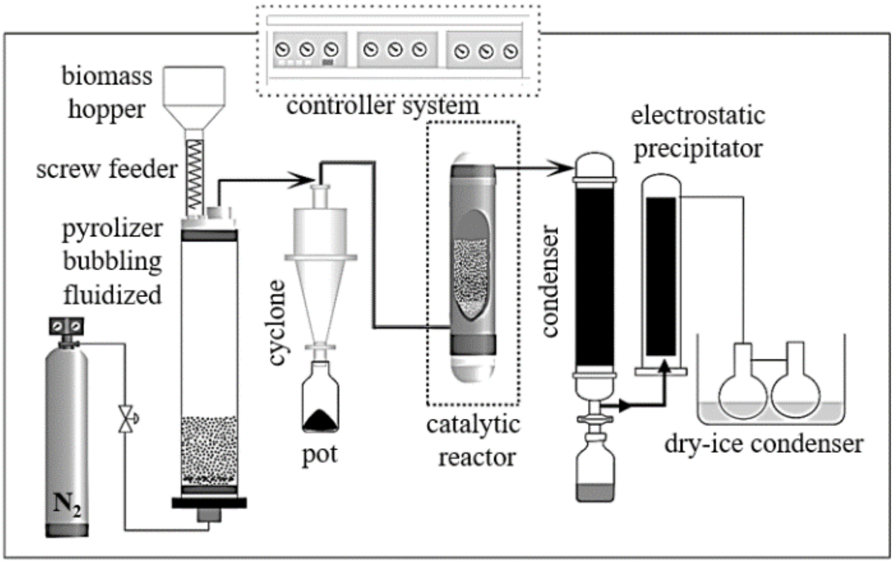

Fig. 1. Schematic diagram of fast pyrolysis

3. RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

The surface morphology of TiO_2 catalyst is presented in Figure 2. Most of the TiO_2 grains exhibited sphere-like shape with uniform grain-size distribution. The SEM image showed agglomeration of the TiO_2 particles indicating a characteristic nature of nanosized particles. Aggregation of the small particles was also observed, possessing similar surface structure. The XRD pattern of the TiO_2 catalyst is presented in Figure 3, showing a diffraction peak pattern corresponding to the standard pattern JCPDS #21-1272. This confirms the existence of crystalline anatase phase in the catalyst. The particle size distribution is shown in Figure 4 demonstrating a bimodal distribution with two spikes at 0.17 µm and 0.23 µm. This finding is consistent with the SEM image in which TiO_2 primary particles and their aggregates were observed. Specific surface area and pore size of TiO_2 catalyst were 124.20 m^2/g and 46.32 Å, respectively. The catalysts with a mesoporous structure afford large pore volume, high specific surface area and high centration of active site per mass, enhancing the mass-transport properties [7].

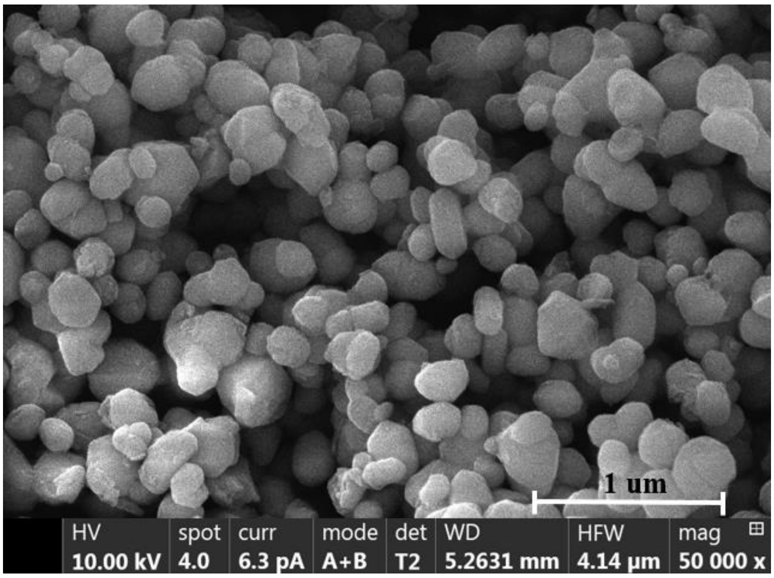

Fig. 2. SEM image of TiO_2 catalyst.

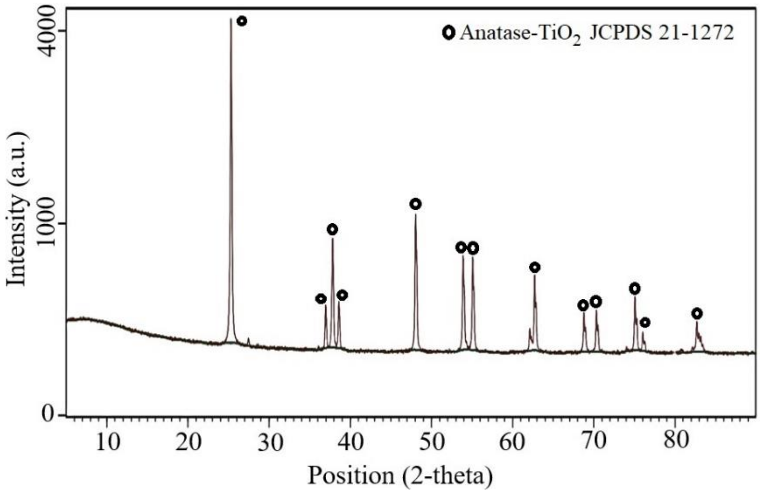

Fig. 3. XRD pattern of TiO_2 catalyst.

FTIR was employed to identify the functional groups and chemical bonds in the catalyst structure. As seen in Figure 5, the spectrum of the TiO_2 catalyst with absorption bands in the range of 500-1250 cm^{-1} was found, which characterized the formation of O-Ti-O lattice. The band at 3422 cm^{-1} was attributed to O-H bond (stretching) of water and the 2919 cm^{-1} and 2850 cm^{-1} band resulted from C-H bond stretching of organic compounds [13]. The 1633 cm^{-1} were attributable to H-O-H bending of hydroxyl group. The absorption bands also appeared at 776 cm^{-1} and 754 cm^{-1} which were caused by Ti-O bond stretching, indicating the presence of anatase phase. Chemical composition was determined using EDX analysis which is presented in Figure 6. The major constituents were Ti and O with approximate percentage of 51.8% and 45.2%, respectively. TiO_2-based catalysts were proved to be a promising alternative used for fast pyrolysis of biomass [4,] [14], [15]. Moreover, EDX elements analysis also detected the presence of C, P, and K (2.4, 0.3, and 0.2, respectively).

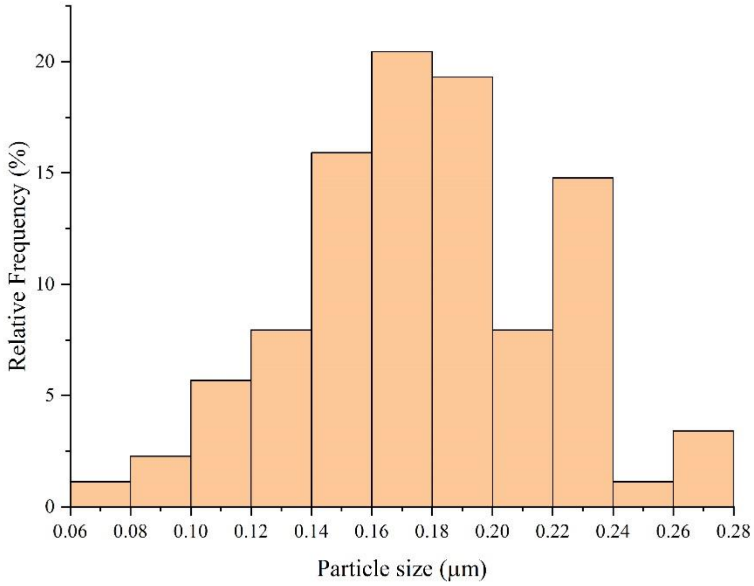

Fig 4. Particle size distribution of TiO_2 catalyst.

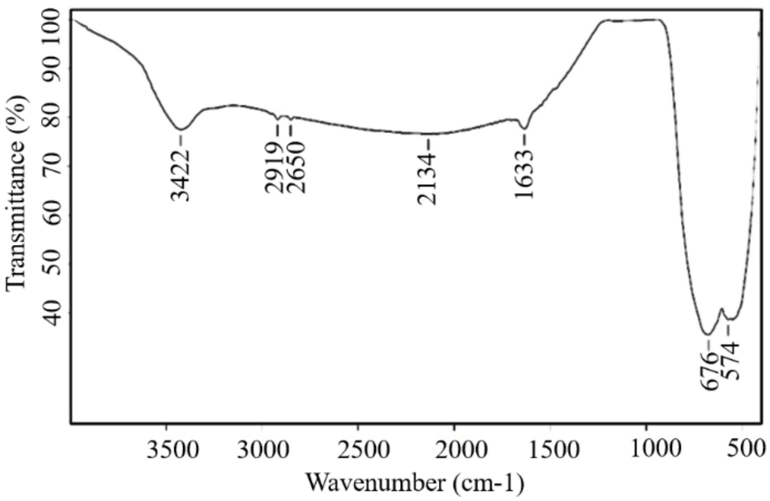

Fig. 5. FT-IR spectra of TiO_2 catalyst.

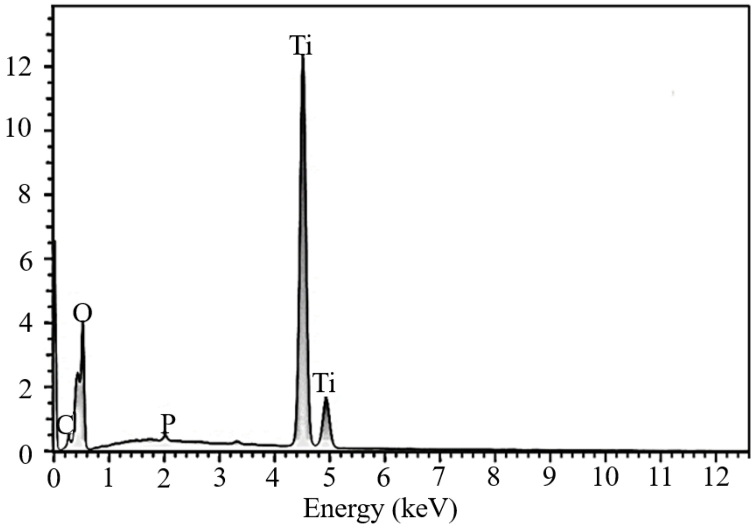

Fig. 6. The EDX image of TiO_2 catalyst.

3.2 Characterization of Feedstock

Leucaena leucocephala were analyzed in terms of physical properties. The bulk density and particle density were 200 kg/m^3 and 679 km/m^3, respectively. The moisture content was reported to be 4.5% w/w with high content of volatile matter (83.7% w/w) and a small residue of ash (1.0% w/w). The fixed carbon content was 12.1% w/w. Regarding ultimate analysis, the carbon and oxygen content were 46.8 %w/w and 45.5 %w/w, respectively. The results also reported that the hydrogen content was 6.0 %w/w higher than nitrogen which was 0.32% w/w. Sulfur was less than 0.02% w/w and the higher heating value (HHV) was 18.2 MJ/kg. The molar O/C and H/C ratios were 0.73 and 1.56, respectively.

3.3 Influence of the Pyrolysis Zone Temperature

It is well known that temperature is considered to be the most influencing parameter on product distribution [16]. Therefore, the influence of pyrolysis temperature in the rage of 400-600°C on the product yields of bio-oil was investigated in order to select the optimal condition for further studies.

Leucaena leucocephala wood was selected as the feedstock in this work because it is an energetic crop and has high growth rate. The first set of pyrolysis test was conducted in the absence of the catalyst by varying the temperature between 400 and 600°C. On completion of the pyrolysis process, the obtained products were weighed and the yields were calculated. The mass yield of the gas was calculated by subtracting the mass of char and bio-oil from the initial mass of biomass feedstock. The results showed that the yield of the pyrolysis products (bio-oil, char, and gas) was dependent on the pyrolysis temperature. As seen in Figure 7, the gas content substantially increased with temperature. However, the bio-oil yield increased with temperature when the pyrolysis temperature was lower than 500°C and it then gradually decreased when the pyrolysis temperature was further increased to 600°C. The decrease of bio-oil yield and the rapid increase in gas phase could be attributed to the breaking down of the pyrolyzed vapors at high temperatures, which is due to secondary cracking reactions. In addition, the char yield was found to decrease with pyrolysis temperature. The results obtained in this work are in good agreement with previous works reported in the literature [15], [17] where the yield of bio-oil was between 42% and 54%. In this work, however, the pyrolysis temperature of 500°C was the best condition to produce the bio-oil with the maximum yield of 54.21% and the HHV of 19.6 MJ/kg. It was also noted that bio-oil yield decreased at temperatures above 500°C was due to secondary thermal cracking reactions of volatile gas [17]. Thus, the optimal temperature, in term of bio-oil yield in the absence of catalyst was 500°C. With regard to the obtained char, the yield markedly decreased from 42% at 400°C to 15% at 600°C. Higher char yields were expected at lower temperatures due to a lower extent of thermal energy together with a major contribution of condensation reactions [18].

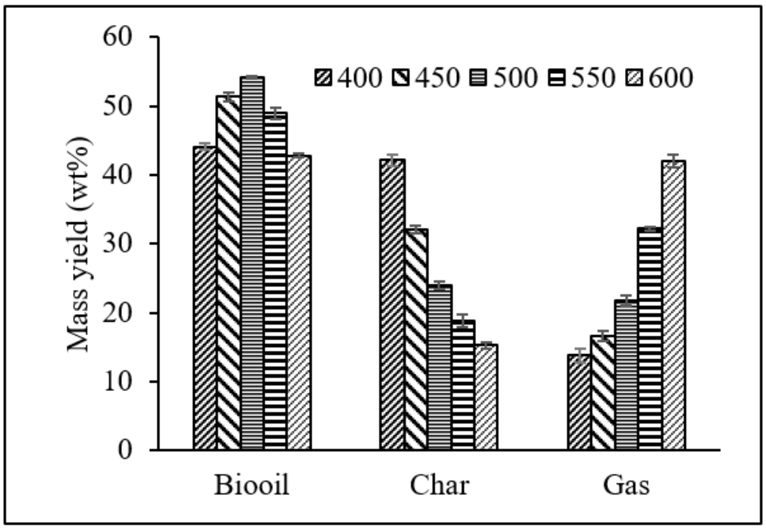

Fig. 7. Effect of pyrolysis temperature on yields of pyrolysis products.

3.4 Influence of the Catalytic Zone Temperature

The effect of the temperature in the catalytic zone was studied at the temperatures ranging from 400 to 600°C using TiO_2/wood = 1:1 catalyst under the pyrolysis zone temperature of 500°C. Figure 8 shows the product yields employing TiO_2 catalyst. The bio-oil yield was found to increase steadily with catalytic temperature, indicating that high catalytic temperatures tended to improve the condensable compounds and consequently produced higher liquid product yield. The bio-oil population reached the maximum value of 59.98% at 600°C. In contrast, the generation of char was about 22%, gas products showed a negative trend, while a little of coke was produced during the pyrolysis.

Figure 9 illustrated the oxygen distribution and the HHV value as a function of the catalytic zone temperature. Compared to the non-catalytic process, the pyrolysis using TiO_2 obtained lower oxygen contents. It was also found to decrease with the catalytic zone temperature. In contrast, the HHV was higher and showed a steady increase with the temperature.

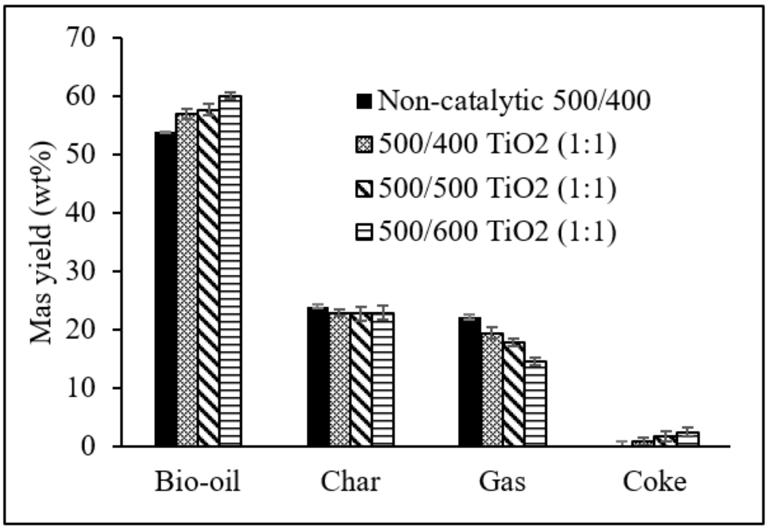

Fig. 8. Effect of catalytic zone temperature on yields of pyrolysis products.

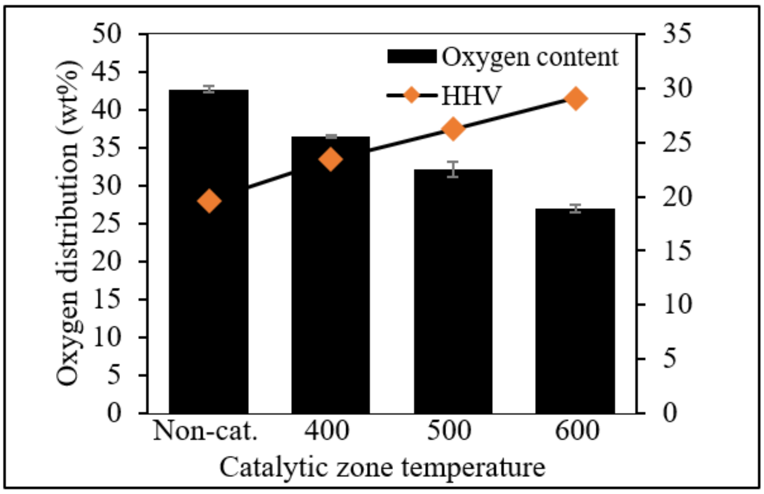

Fig. 9. Effect of catalytic zone temperature on oxygen content and the HHV of bio-oil product.

The chemical reactions involving the removal of oxygen element in oxygen-containing functional groups in the form of H_2O, CO, and CO_2 was explained in Equations 1 to 3 [19].

Dehydroxylation reaction: R-OH → R_1+H_2O (1)

Decarbonylation reaction: R-COH→R-H+CO (2)

Decarboxylation reaction: R-COOH→R-H+CO_2 (3)

In conclusion, oxygen content in bio-oil could be reduced through decarboxylation reaction promoted by the application of TiO_2 catalyst and higher temperatures, thus increasing the HHV of bio-oil.

3.5 Influence of the T/W Mass Ratio

Different T/W ratios ranging from 1:1 to 3:1 was applied to investigate the catalytic performance of TiO_2. All the experiments were carried out using the same condition in which pyrolysis and catalytic zone temperature were 500 and 600°C, respectively. The effect of catalyst dosage on product yield is shown in Figure 10. In the absence of the catalyst, bio-oil yield of approximate 54% was obtained. When the catalyst was used, the bio-oil yield exhibited a steady increase with the catalyst dosage. The yield of bio-oil was 59.98% when the T/W ratio of 1:1 was used. It could increase up to 67.10% when the T/W was 3:1. Moreover, an increase in catalyst loading had a good effect on the release of gases. The gas yield markedly decreased by more than 50% with increasing the catalyst loading to 3:1 compared to 1:1. The oxygen content decreased from 27.1% to 24.5% with the use of 3:1.

The catalytic pyrolysis produced bio-oil with lower oxygen contents and higher HHVs compared to pyrolysis without the catalyst. Additionally, as seen in Figure 11, the oxygen content dropped dramatically from 42.5% to 26% when TiO_2 was applied in the pyrolysis. However, increasing the T/W ratio led to a slight decrease. In contrast to the oxygen content, the HHV markedly increased from 25% to 37% when the 1:1 T/W catalyst was used. Nevertheless, no significant effect was observed when the T/W ratio was increased from 2:1 to 3:1.

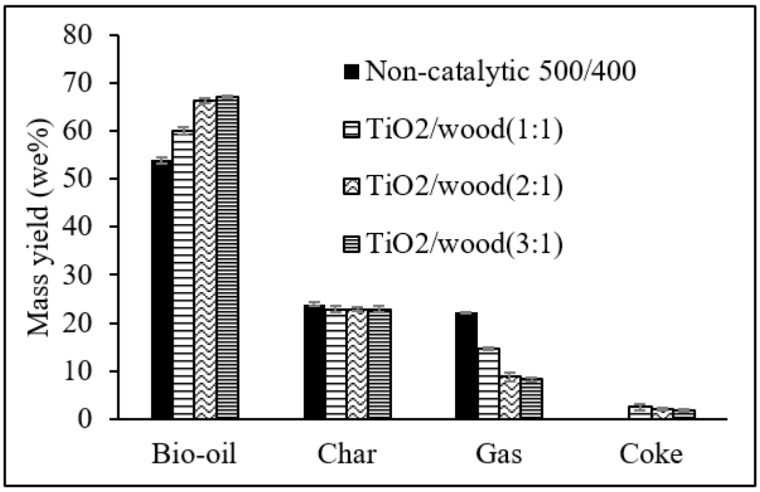

Fig. 10. Effect of T/W ratio on yields of pyrolysis products.

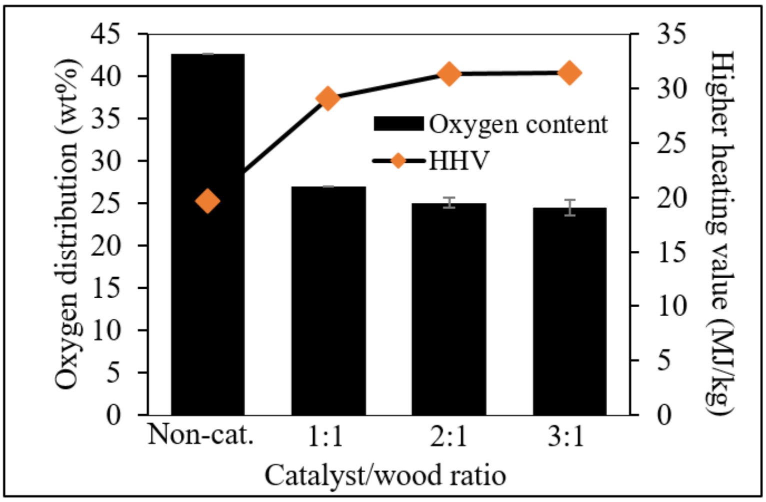

Fig. 11. Effect of T/W ratio on oxygen content and the HHV of bio-oil product.

Table 1. The properties of the best bio-oil obtained in this work.

Property	ASTM D7544-12	This work
Water content, wt%	≤30	8.1 ± 1.2
Solid content	≤2.5	0.24 ± 0.03
Kinematic viscosity, cSt @ 40°C	≤125	11.42 ± 0.9
Density, kg/dm^3	1.1-1.3	1.2 ± 0.1
Sulfur content, wt%	≤0.05	0.015 ± 0.004
Ash content, wt%	≤0.25	0.98 ± 0.12
pH	-	4.20 ± 0.11

The best bio-oil produced in this study was derived through the pyrolysis at 500°C under the catalytic zone temperature at 600°C using 3:1 T/W catalyst. Its HHV was 31.5 MJ/kg. Its properties were also characterized according to ASTM D7544-12. As clearly seen in Table 1, the bio-oil met the standard suggested by ASTM D7544-12 "Specification for Pyrolysis Liquid Biofuel".

4. CONCLUSION

The experimental study on biomass catalytic pyrolysis decoupling the pyrolysis and catalytic zone was conducted to evaluate the effect of three key parameters temperature of pyrolysis zone, temperature of catalytic zone, and the T/W ratio. TiO_2 catalyst was applied for upgrading vapors generated from the pyrolysis of *Leucaena leucocephala* in terms of bio-oil yield and the HHV and the oxygen content. It was found that an increase in the pyrolysis zone temperature led to a higher yield of bio-oil and a lower yield of char and gas. However, bio-oil yield gradually decreased with the pyrolysis temperature above 500°C. The pyrolysis temperature of 500°C resulted in the maximum yield of 54.21%. Regarding the effect of catalytic zone temperature, an increase of the temperature provoked a progressive creation of bio-oil yield leading to enhancement of the HHV with a low level of oxygen content. The T/W ratio ranging from 1:1 to 2:1 caused an abrupt increase of bio-oil yield, while increasing T/W ratio from 2:1 to 3:1 caused a linear increase of bio-oil yield and the HHV. Bio-oil yield reached the maximum at 67.1% with the lowest oxygen content of 24.5%. The bio-oil obtained in this work satisfied the ASTM D7544-12 standard, implying the use of the catalytic pyrolysis is possible for improving the quality and productivity of bio-oil product.

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