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A Study on Better Temperature of Anoxic Pyrolysis Process in Oil Palm Kernel Shell Treatment Plant

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Keywords：Pyrolysis, Bio-char, Bio-oil, Bio-gas

ABSTRACT

The pyrolysis process is one of the thermal treatment method for biomass. This study adopted a low energy consumption, mass-producible anoxic pyrolysis process with a controlled temperature of 500 and 550˚C, comparing their different influences on the products rate from the pyrolysis of oil palm waste kernel shell, so as to search for the better pyrolysis process in order to produce more high-value pyroligneous acid and biogas.

INTRODUCTION

Origin of Palm Oil

Palm oil is a vegetable oil derived from the fruit of the oil palms. About 5000 years ago, people in Africa already began to extract such oil from the fruit of oil palms (Mukherjee and Analava, 2009). Later, the oil palm was introduced to countries in Southeast Asia for cultivation. Currently, the major palm oil producers in the world are Indonesia and Malaysia, while Colombia is the fourth largest palm oil producer in the world.

Oil palm is originated from the west coast of Africa. In the 1970s, countries in Southeast Asia began to plant large quantities of oil palms. In the 1980s, the planted area of oil palm and the production of oil palm fruit in Southeast Asia had exceeded that in Africa. Since the 1970s, palm oil production has shown the fastest growth among various vegetable oils, and has become one of the major edible oils in the world, accounting for a major portion of the international vegetable oil market.

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Production of Palm Oil

According to the statistics of the Food and Agriculture Organization of the United Nations (2015), the total production of oil palm fruit worldwide has shown rapid growth every year since 1981, and the production in 2017/2018 was as high as 69.33 million tons. According to the statistics, the total oil production worldwide in 1992 was 84.7 million tons and it reached 187 million tons in 2013 (Mielke, 2014), showing a growth rate of more than 2 times. Furthermore, the production of palm oil in 2013 accounted for 30% of the total oil production, and the consumption of palm oil in the food industry has increased rapidly year by year, making it the world's most demanded oil (Untied States Department of Agriculture, 2015, 2020).

Palm Oil Production Process

Oil palm can reach its harvest period 3 years after planting, and has an economic lifetime of 25 years. Oil palm fruits grow in bunches, with approximately 2,000 fruits in each bunch. Each bunch weighs about 10 to 20 kg. Each fruit is composed of pulp and nut (seed) that contain different amounts of oil. Tenera pulp (the major type of oil palm planted in Malaysia) contains about 49% palm oil while the nut contains about 50% palm kernel oil. Each hectare of oil palm can produce approximately 4.0 tons of palm oil, 0.5 ton of palm kernel oil (PKO) and 0.6 ton of palm kernel meal (PKM). Compared with other oil crops, oil palm produces the most oil per hectare (Taiwantrade, 2020). One hectare of soybean can produce 400 kg of soybean oil, while one hectare of oil palm can produce 4,000 to 8,000 kg of palm oil.

Bio-waste and Its Treatment

During the growth of oil palm, matured oil palm fruits are cut in bunches manually, collected manually or by machines, and then transported to oil mill by truck to carry out the oil extraction process as shown in Figure 1. From the growing of oil palm to the oil extraction process, some biomass waste (bio-waste) will be generated, each ton of palm oil produced will generate nearly five tons of waste. With the increase of palm oil demand, the generation of these palm oil mill wastes also increases. Malaysia's oil palm waste will increase from the current 85 million tons to 110 million tons in 2020 (AgensiInovasi Malaysia, 2013; Materialsnet, 2020). Some smaller or less skilled oil mills can only produce 2 tons of crude palm oil per 40 tons of palm fruits, suggesting that for every ton of crude palm oil produced, 19 tons of bio-waste such as hollow palm fruit clusters or palm fruit husks will be generated (Rosner et al., 2020). It is estimated that the palm oil production worldwide in 2020 will reach at least 74 million tons. By taking the ratio of 1:5, it is projected that about 370 million tons of bio-waste will be generated worldwide in 2020 due to the production of palm oil. If these wastes are not properly treated and are allowed to decompose naturally via composting, they will release large amount of greenhouse gases such as CO_2, CH_4 and N_2O due to the lack of oxygen in the bottom layer of the compost. Especially for CH_4 and N_2O, since their global warming potential (GWP) is 14 and 296 times that of CO_2, with increasing danger to the environment. For this reason, bio-waste from palm oil production should be reutilized to avoid the generation of greenhouse gases.

Collection of palm fruits
↓
Disinfection
↓
Separation by tapping
↓
fruit husks ← fruit milling → crude oil sieving
↓ ↓
Nut (kernel) Refining
↓
Pressing → Kernel waste
↓
Palm kernel oil

Fig. 1. Palm oil extraction and bio-waste generation processes (Materialsnet, 2020)

Currently, there are many ways to reutilize the waste generated from processing of oil palm fruit (and kernel), including production of biofuel, bio-feed, bio-fertilizer, bio-charcoal, and sugar production from extraction and fermentation, etc., and some of them have already been implemented in large scale. For example, large-scale palm oil production plants have directly used the crushed wastes from palm oil production as fuel for boilers, or dried and grinded the pulp with certain oil content after oil extraction as feed ingredients. Some operators convert the wastes into organic fertilizers via composting while others turn them into biofuel pellets (rods) (Yek and Ogawa, 2017; Louisa, 2017). Bio-char and sugar production from fermentation, on the other hand, have not yet been implemented in large scale.

Biomass Pyrolysis

Pyrolysis is a process for heating the material in a low-oxygen (hypoxic) or anoxic environment. Since the material is heated under low-oxygen or anoxic condition, combustion will not take place abundantly. Instead, decomposition and evaporation of organic substances will occur majorly. Biomass pyrolysis process can be divided into slow pyrolysis and fast pyrolysis. Slow pyrolysis produces 35% bio-char, 30% bio-oil and 35% biogas in relation to the raw material (Jakab et al., 2000), while fast pyrolysis produces about 15% bio-char, 70% bio-oil and 13% biogas (McCarl et al., 2009). The combination of end products from pyrolysis depends on various parameters including temperature, retention time, raw material, reactor configuration, heating rate, working pressure and catalyst added (Demirbaş and Arin, 2002; Yan et al., 2005; Sukiran, 2008; Kherbouche and Benyoucef, 2011).

For example, the pyrolysis of wood at 400 ℃ is an endothermic process, and its reaction is as follows (Antal and Grønli, 2003):

$$\text{(Wood) Biomass}\ (2C_{42}H_{60}O_{28}) + \text{Heat} \rightarrow \text{Tar/biooil}\ (C_{28}H_{34}O_9) + \text{Biogas}\ (28H_2O + 5CO_2 + 3CO) + \text{Biochar}\ (3C_{16}H_{10}O_2)$$

In this reaction, the pyrolysis furnace temperature and the retention time are the most critical parameters of the operation (Chen et al., 2003; Kim et al., 2010). The increase in the final temperature and the retention time will increase the gasification volume of the solid, hence, reducing the amount of biochar generated at the end (Lua and Guo, 1998; Khor et al., 2009; Razuan et al., 2010). When the temperature is increased to 500 ℃, maximum biooil production can be achieved. However, as the temperature is further increased, the biooil production decreases (Sukiran, 2008; Kim et al., 2010), while the volatile biogas production increases (Yan et al., 2005; Khor et al., 2009; Yang et al., 2006). Biogas is mainly composed of H_2, CO_2, CH_4 and CO (Yan et al., 2005; Razuan et al., 2010; Mohammed et al.; 2011). The yield of H_2 and CO increases with increasing temperature, while the yield of CO_2, CH_4 and H_2O decrease with increasing temperature. Moreover, when the temperature exceeds 800 ℃, the yield of CO_2, CH_4 and H_2O drops to zero (Yan et al., 2005; Yang et al., 2006).

Currently, there are some laboratory studies on the pyrolysis of biowaste generated from the oil extraction of palm fruit or kernel (Lua and Guo, 1998; Kim et al., 2010; Khor et al., 2009; Razuan et al., 2010; Yang et al., 2006; Abdullah et al., 2008; Thomsen et al., 2011; Lua et al., 2006; Sukiran et al., 2009; Abdullah et al., 2010; Abdullah et al., 2011). However, studies on mass-producible pyrolysis plant are rarely found. This study conducted investigation on the temperature conditions and products of the oil palm kernel shell pyrolysis process for a newly-constructed mass-producible plant (YD Lt. Com.) in Taiwan. The product yield, heating value and changes in composition were analyzed, serving as the reference for better temperature operation.

MATERIALS AND METHODS

Oil Palm Kernel Shell

The oil palm kernel shells imported from Indonesia (were dried first) are shown in Figure 2 (the shells had irregular sizes, most of which had length and width between 5 and 10 mm). They were placed in the feed storage area for later use. Sampling of the oil palm kernel shells was conducted to determine their physical and chemical properties as shown in Table 1. From Table 1, it is noted that the moisture content of the oil palm kernel shell after drying is reduced to 11.4% (its moisture content after oil extraction and before drying is more than 80%). The oil content is 0.44%, and the flash point is 135 ℃. The higher heating value of the dry basis reaches 4608 kcal/kg, and the ash content after complete combustion is as low as 2.51%. This suggests that most of the materials are flammable and can serve as good fuels.

Fig. 2. Oil palm kernel shells after drying (source: Yuan Da Technology Co., Ltd.)

Table 1. Physical and chemical properties of dried oil palm kernel shells

Analysis item	Measured value	Method
Ash	2.51 %	ASTM D482
Moisture (105℃, 3hr)	11.4%	Gravimetric method
Oil content	0.44%	ASTM D3495
Flash point	135℃	ASTM D92 as reference
Dry basis higher heating value	4608 Kcal/kg	ASTM D240

Pyrolysis Process and Operation

The pyrolysis plant is located in Tainan City, Taiwan. The plant area is about 1600 m^2, which is divided into feed storage area, process area and product storage area. The units in the process area include a low-oxygen pyrolysis furnace (or gasifier), water scrubber and distillation tank. The process flow is shown in Figure 3. The oil palm kernel shells with weight about 300±10 kg were first sent into a low-oxygen pyrolysis furnace with a volume of about 0.8 m^3 by conveyor belt. The top of the furnace was covered to avoid air inflow after feeding. The furnace was ignited to raise the temperature to 500±10 ℃ or 550±10 ℃ within 15-20 minutes, carrying out the anoxic high-temperature pyrolysis process. The raw biogas produced was pumped into two water scrubbers with volume of approximately 55 and 1100 liters each through the gas pipe at that side of the furnace (with pumping rate of about 25 m^3/min). The biogas was then condensed by the cooling water to produce the biooil-water mixture. The biooil-water mixture was placed into a circulating water tank with a volume of 1200 liters for circulating condensation. After 25 feeds of oil palm kernel shells (a total weight of 7.5 tons), the tank was replaced with fresh condensate, and the biooil-water mixture was discharged into the biooil-water storage tank. The mixture then underwent the distillation process to obtain pure pyroligneous acid and concentrated biooil. The concentrated biooil can be returned to the anoxic pyrolysis furnace for repeated pyrolysis. The gas after passing the water scrubber is regarded as pure biogas, which was sent to be stored in the gas storage tank, and then pumped to the furnace bottom for incineration and heating the furance. The oil palm kernel shells in the pyrolysis furnace after smoldering gradually turned into biochar, which was then pushed to the bottom outlet pipe by a rotator in the furnace and dropped into the spiral delivery pipe under the furnace to leave the furnace. The biochar was then delivered to the product storage area by a conveyor belt and cooled naturally to form the biochar product.

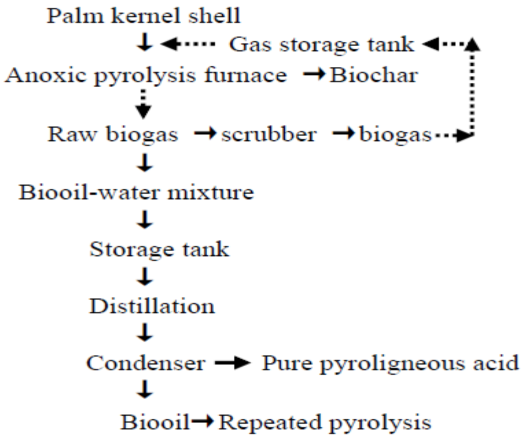

Fig. 3. Process flow of the mass-producible pyrolysis plant for oil palm kernel shells (source: Yuan Da Technology Co., Ltd.)

Analysis Method and Equipment

The sampling of oil palm kernel shells or biochar for analysis was conducted by collecting approximately 1 L of sample from 3 random places in the feed storage or finished product storage, and then mixed the three 1-L samples uniformly. One liter of the mixed sample was then used to carry out analysis in the laboratory.

The physical and chemical properties of the oil palm kernel shells, biochar or biogas analyzed in this study include moisture, ash, combustibles, volatile organic compounds, fixed carbon, nitrogen, carbon, hydrogen, sulfur, heating value, apparent density, and iodine value. The analysis adopted the NIEA methods announced by the Taiwan EPA (Environmental Protection Administration) or the US ASTM methods, and the equipment used was required by the corresponding method were shown in Table 2. Biochar produced under different temperature conditions of the pyrolysis plant was sampled and delivered to different or appropriate laboratories for analysis. Each measurement was repeated twice and the average of the two measurements was used as the final result for analysis to increase reliability.

Table 2. Analysis method and equipment for oil palm kernel shells, biochar and biogas

Analysis item	Analysis method and equipment
Moistures	NIEA R205.01C Oven and High-temperature furnace
Ash	
Combustibles	
Volatile matters	ASTM D3172-13 Oven and High-temperature furnace
Fixed carbon	
N	Elementary Analyzer Crusher and sieve Balance
C	
H	
S	

Table 2. (cont.)

Analysis item	Analysis method and equipment
Heat values	NIEA R214.01 Crusher Bomb calorimeter (for biochar and biooil), water flow calorimeter (for biogas)
Apparent density	Volumetric weight method Balance
Iodine value	ASTMD4607-94 Crusher and sieve

RESULTS AND DISCUSSIONS

Temperature and Product Yield

In this study, the oil palm kernel shells were pyrolyzed in the pyrolysis furnace at temperatures of 500 and 550℃ separately. The generated biochar after pyrolysis is shown in Figure 4. The biochar has different sizes, with length and width ranging from 2 to 10 mm, and an average of about 5~6 mm. The temperatures of the pyrolysis furnace at 500 and 550 ℃ seem to have no significant impact on the size of the biochar. The average yields of all products (after cooling to room temperature) generated from the pyrolysis are as follows: 0.28~0.30 tons of biochar, 0.48~0.54 tons of biogas and 0.18~0.22 tons of biooil-water mixture (biooil). Figures5(a)~(c) show the average yields of all three products (biochar, biooil-water mixture, and biogas) at different pyrolysis furnace temperatures. Figures 5(a) and (b) show that the yields of biochar and biooil-water mixture decreases as the temperature is increased from 500°C to 550°C. However, Figure 5(c) shows an opposite trend; the yield of biogas increases as the temperature is increased from 500°C to 550°C.

Fig. 4. Biochar generated after the pyrolysis of oil palm kernel shells (source:Yuan Da Technology Co., Ltd.)

The product yields in this study are compared with those from other studies as shown in Table 3. The product yields and the trend obtained in this study are different from those of slow pyrolysis (Jakab et al., 2000) and fast pyrolysis (McCarl et al., 2009). However, they are closer to the trend of slow pyrolysis. In this study, the pyrolysis furnace was heated to the highest temperature in about 20 minutes, and was maintained at such temperature for about 40 minutes, with a total period of about 1 hour. This long pyrolysis period may be regarded as slow pyrolysis. The correlation between product yield and temperature observed in this study is consistent with that described in other studies (Yan et al., 2005; Sukiran, 2008; Chen et al., 2003; Kim et al., 2010; Lua and Guo, 1998; Khor et al., 2009; Razuan et al., 2010; Yang et al., 2006). Therefore, if one wants to generate more biogas, the pyrolysis of oil palm kernel shells should be carried out at 550°C. On the other hand, if one wants to generate more biochar and biooil, the pyrolysis furnace should be operated at 500°C. In addition, the biooil in this study was obtained via water scrubbing which produces a mixture of biooil and water, while the biooil in other studies was obtained via air-cooling condensation. Since the methods adopted are different, the results may be different. However, the rate of generating biooil by water scrubbing is faster than that by air cooling. Furthermore, it minimizes the length of the gas cooling pipe to reduce the cost of equipment. Both are the merits of this process.

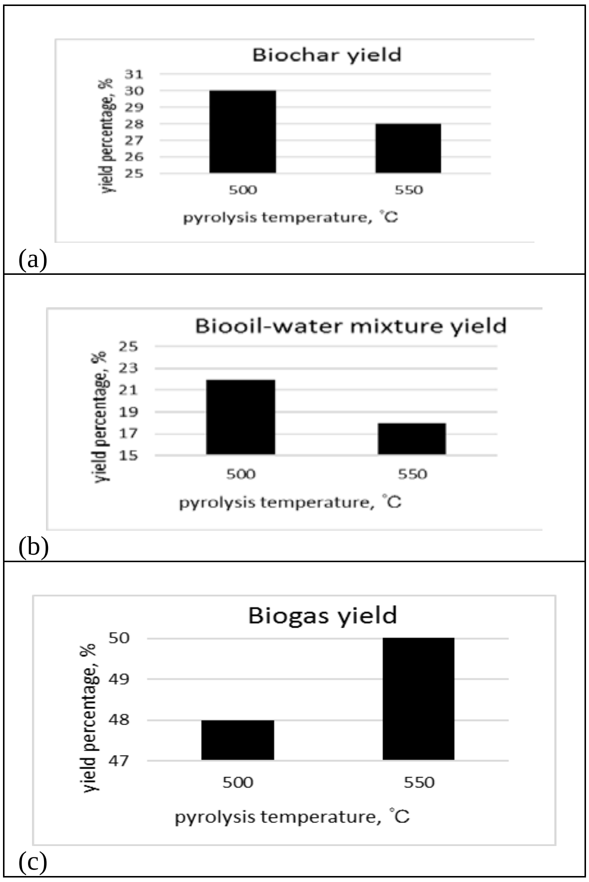

Fig. 5. Comparison of average 3 products yields under different pyrolysis temperatures (source: Yuan Da Technology Co., Ltd.)

Table 3: Product yields under different pyrolysis temperatures (source:Yuan Da Technology Co., Ltd.)

Pyrolysis temperature, ℃		500	550	Slow pyro-lysis (Jakab et al., 2000)	Fast pyro-lysis (McCarl et al., 2009)
Product yield,% (room temp.)	Biochar (average)	30	28	35	15
	Biooil-water mix. (average)	22	18	30	70
	Biogas (balance)	48	54	35	13

Pyrolysis Temperature and Biochar Composition

Properties and composition of the biochar were further analyzed including moisture, combustibles, volatile substances, fixed carbon, nitrogen, carbon, hydrogen and heating value. The results under different pyrolysis furnace temperatures (500 and 550 ℃) were compared as shown in Figures 6(a)~(h). From Figures 6(a)~(h), it is noted that the percentages or values of moisture, combustibles, volatile substances, fixed carbon, nitrogen, carbon, hydrogen and heating value of the biochar generated at 500 ℃ are all higher than those of the biochar generated at 550 ℃; the ratio of the high and low percentages (high/low, %) or values (high/low, kcal/kg, dry basis higher potential) for moisture, combustibles, volatile substances, fixed carbon, nitrogen, carbon, hydrogen and heating value are 14.98/13.53, 74.87/69.08, 21.15/18.87, 81.13/78.85, 0.44/ 0.40, 75.15/73.39, 1.67/1.62, and 7400/7100, respectively. The results suggested that under higher pyrolysis temperature of 550 ℃, more organic substances were decomposed and evaporated. Consequently, the organic content remaining in the biochar is reduced, resulting in lower yield of the biochar as well as other products and lower heating value. Such finding was not mentioned in other studies. Therefore, this process can be operated by controlling the pyrolysis furnace temperature based on the purpose of operation or product requirements.

The properties of biochar which have opposite trend to that in Figures 6(a)~(h) are apparent density and ash content. Figures 7(a) and (b) show respectively the apparent density and ash content of biochar generated at different temperatures. At the pyrolysis temperature of 500 ℃, the apparent density and ash content of biochar is 0.72 g/cm^3 and 10.15%, respectively, which are lower than the apparent density (0.76 g/cm^3) and ash content (17.39%) of biochar generated at pyrolysis temperature of 550℃. This suggests that at the pyrolysis temperature of 550 ℃, the organic contentin the biochar is relatively small (as shown in Figures 6(c), (e), (f), and (g)) and the inorganic component is relatively large, resulting in higher apparent density and ash content.

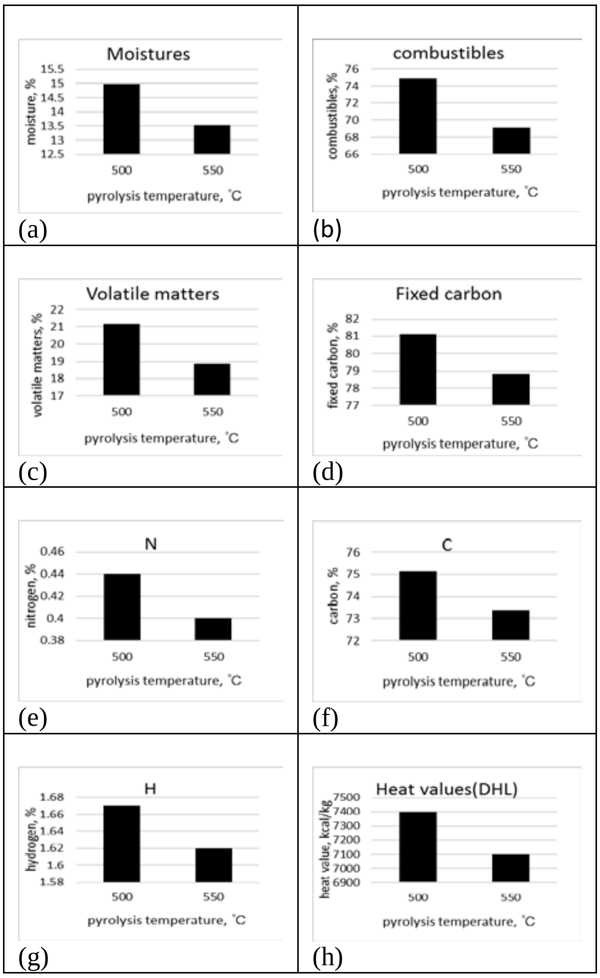

Fig. 6. Properties and composition of the biochar generated at different pyrolysis temperatures

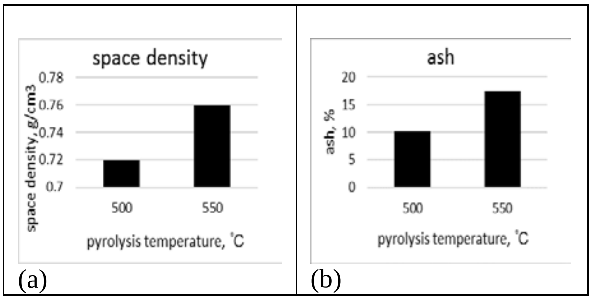

Fig. 7. Apparent density and ash content of biochar generated at different pyrolysis temperature

Biogas

The gaseous biogas after being condensed to room temperature was sampled by a 10-liter gas collecting bag, and its density was analyzed by volumetric weight method, which is about 1.10~1.25 kg/m^3. Its heating value was then analyzed by a water-flow calorimeter. The heating value of the biogas is related to the moisture content and the pyrolysis temperature of the oil palm kernel shell. When the moisture content of oil palm kernel shell is 18% and the pyrolysis temperature is 500℃, the heat value of the generated biogas is only about 3500~4000 kcal/Nm^3 (high level value,dry basis). When the moisture content of oil palm kernel shell is 15±1% and the pyrolysis temperature is 500℃, the heatvalue of the generated biogas is about 5300~5500 kcal/Nm^3, while at the pyrolysis temperature of 550 ℃, the heat value of the generated biogas is about 5500~5700 kcal/Nm^3. When the moisture content of oil palm kernel shell is below 10% and the pyrolysis temperature is 550℃, the heat value of the generated biogas can reach as high as 7041 kcal/m^3 (high level value, dry basis). This indicates that the lower the moisture content of the oil palm kernel shell, the higher the heating value of the generated biogas can be obtained from the pyrolysis. Furthermore, the higher the pyrolysis temperature for the oil palm kernel shell, the higher the heat value of the generated biogas can be obtained from the pyrolysis. Therefore, oil palm kernel shells with lower moisture content should be used for pyrolysis in order to obtain higher heat value for the generated biogas. After being condensed and cooled, the generated biogas can be delivered to a gas generator for burning to generate power, which is used by the lighting and electrical appliances in the factory area.

Biooil and Pyroligneous Acid

The biooil-water mixture produced in this process was distilled to produce 0.02-0.03 tons of concentrated biooil and 0.15-0.20 tons of pure pyroligneous acid. Biooil is the oil remaining in the shell of palm kernel after oil extraction. Its heat value was analyzed by a calorimeter, which is about 6000~6500 kcal/kg. After sufficient amount of biooil is being collected and stored, it can be returned to the pyrolysis furnace for reprocessing to produce biogas, or used as a fuel.

Pure pyroligneous acid is natural organic lignin; therefore, its heat value is very low and can be ignored. Its organic content is about 2.5~6.5% (mainly acetic acid and phenolic ingredients). Its pH value is about 3.1~4.2 and it can be used for as fungicidal (antifungal) and antibacterial agent in agricultural applications. It is also a natural pesticide (Yongyuth et al., 2020; Zainab et al., 2020). In recent years, it has been found that pyroligneous acid also has anti-inflammatory and antioxidant effects for the human body (Zainab et al., 2020). In order to expand its use, dipotassium hydrogen phosphate was added into the pyroligneous acid, making the mixture as a liquid fertilizer. Therefore, if one wants to produce more pyroligneous acid, the process should be conducted at the pyrolysis temperature of 500 ℃ or using fast pyrolysis (McCarl et al., 2009).

CONCLUSIONS AND SUGGESTIONS

In this study, mass-producible anoxic pyrolysis process with water scrubbing condensation was adopted. The temperature of the pyrolysis furnace was controlled at 500 or 550℃ (± 10 ℃). In this process, 0.6~0.7 ton of oil palm kernel shells can be pyrolyzed per hour. For every ton of oil palm kernel shell pyrolyzed, the process can generate 0.28~0.30 ton of biochar, 0.18~0.22 ton of biooil-water mixture (0.15~0.20 ton of pure pyroligneous acid and 0.02~0.03 ton of biooil after distillation) and 0.48~0.54 ton of biogas. The product yield is close to the rate of slow pyrolysis as mentioned in the literatures. If one wants to produce more biogas, the pyrolysis furnace should operate at 550 ℃. If one wants to produce more biochar and biooil-water mixture, the pyrolysis furnace should be operated at 500 ℃. The percentages or values of moisture, combustibles, volatile substances, fixed carbon, nitrogen, carbon, hydrogen and heat value of the biochar generated at furnace temperature of 500 ℃ are higher than those generated at furnace temperature of 550 ℃.

Operating the pyrolysis furnace at a faster temperature rising rate can create the condition similar to that of the fast pyrolysis as described in the literature, which may generate nearly 70% of biooil and about 15% of biochar and biogas. However, faster temperature rising rate was not adopted in this study to carry out the pyrolysis operation. When operating the pyrolysis furnace in batches, faster temperature rising rate will consume more energy, require more expensive insulation materials, and cause more damage to equipment due to the repeated cooling expansion of the steel structure of the equipment.

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廢棕櫚仁殼廠缺氧熱裂解產物之佳化溫度研究

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摘 要

熱裂解製程是一種生物質之熱處理方法，本研究採用低能耗、可大規模生產的缺氧熱裂解製程，比較熱裂解爐溫度控制在 500 或 550°C對所得產品產率之影響，作為控制廢棕櫚仁殼熱裂解製程之依據，以產生更多高價值的木醋液和生質氣(能)產品。