



**Production and Characterization of Biochar and Liquid Product from
Slow Pyrolysis of Durian Peel**

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**A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Energy Technology
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from Slow Pyrolysis of Durian Peel

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บทคัดย่อ

เปลือกทุเรียนเป็นชีวมวลประเภทหนึ่งที่ได้จากวัสดุเหลือใช้ทางการเกษตรซึ่งมีปริมาณมากในประเทศไทย งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาคุณสมบัติทางความร้อนและเคมีของเปลือกทุเรียนพื้นเมือง 3 ชนิด ได้แก่ หมอนทอง พวงมณี และบาเจาะ รวมถึงลักษณะของไบโอชาร์และน้ำส้มควันไม้ ที่ได้จากการไพโรไลซิสอย่างช้าของเปลือกทุเรียน จากการศึกษาพบว่าเปลือกทุเรียนหมอนทองมีปริมาณสารระเหยและคาร์บอนคงที่มากที่สุดคือร้อยละ 73.97 และ 18.43 โดยน้ำหนักตามลำดับ จากนั้นมีการศึกษาการเปลี่ยนเปลือกทุเรียนเป็นไบโอชาร์และน้ำส้มควันไม้ผ่านการไพโรไลซิสแบบช้า การออกแบบของค์ประกอบส่วนกลาง (Central composite design, CCD) ถูกนำมาใช้เพื่อออกแบบสภาวะของตัวแปรอิสระสามตัว ได้แก่ อุณหภูมิไพโรไลซิส อุณหภูมิควบแน่น และระยะเวลาในการไพโรไลซิส พบว่ามีเพียงอุณหภูมิไพโรไลซิสที่มีอิทธิพลอย่างมากต่อร้อยละผลได้ของไบโอชาร์และน้ำส้มควันไม้ โดยการวิเคราะห์ความแปรปรวน ร้อยละผลได้ของไบโอชาร์และน้ำส้มควันไม้มีความเหมาะสมกับแบบจำลองพหุนามอันดับสองที่สอดคล้องกับผลการทดลอง เมื่ออุณหภูมิของการไพโรไลซิสเพิ่มขึ้น ร้อยละผลได้ของผลิตภัณฑ์ที่เป็นของแข็งจะลดลง ในขณะที่ร้อยละผลได้น้ำส้มควันไม้เพิ่มขึ้น ร้อยละผลได้ของไบโอชาร์และน้ำส้มควันไม้สูงสุดคือร้อยละ 56.11 และ 38.53 การตรวจสอบความถูกต้องของแบบจำลองจากการทำนายทั้งสองสมการ แสดงให้เห็นความสอดคล้องมากกว่าร้อยละ 96 ซึ่งได้ไบโอชาร์ที่มีค่าความร้อนสูง 26.55 MJ/kg จากการวิเคราะห์โดยใช้กราฟ Van Krevelen อัตราส่วนโมลาร์ของ H/C และ O/C ของถ่านชีวภาพที่อุณหภูมิไพโรไลซิส 600 °C มีความคล้ายคลึงกับวัสดุถ่านหิน อีกทั้งถ่านชีวภาพคุณภาพสูงที่ได้จากการทดลองอยู่ในชั้นกักเก็บคาร์บอน 4 ตามการจัดประเภท IBI และคุณสมบัติของผลิตภัณฑ์ของเหลวเป็นไปตามมาตรฐานผลิตภัณฑ์ชุมชนของประเทศไทย นอกจากนี้ยังมีการวิเคราะห์ทางเศรษฐศาสตร์เพื่อประเมินความเป็นไปได้ของการเปลี่ยนเปลือกทุเรียน 60 ตันต่อปี ให้เป็นถ่าน

ชีวภาพและผลิตภัณฑ์ของเหลว มีการประมาณอัตราผลตอบแทนโครงการภายใน (IRR) ที่ร้อยละ 25.91 โดยมีระยะเวลาคืนทุน 1.58 ปี การค้นพบของการศึกษานี้บ่งชี้ถึงความเป็นไปได้ทางเศรษฐกิจของการนำการไฟโรไลซิสขนาดใหญ่ไปใช้โดยใช้ของเสียจากการเกษตร

คำสำคัญ: เปลือกทุเรียน, ไบโอดีเซล, น้ำส้มควันไม้, การไฟโรไลซิสแบบช้า, สถิติเชิงวิเคราะห์, การวิเคราะห์ทางเศรษฐศาสตร์

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ABSTRACT

Durian peel is a type of biomass derived from agricultural residues, which are found in abundant in Thailand. This study aims to investigate the thermal and chemical properties of three indigenous durian peels, namely Monthong (MDP), Puangmanee (PDP), and Bacho (BDP), as well as the characteristics of biochar and pyrolysis liquid derived from slow pyrolysis of the durian peel. MDP had the greatest volatile matter and fixed carbon content, with 73.97 and 18.43 wt.%, respectively. The central composite design was utilized to optimize the conditions of three independent variables, namely pyrolysis temperature, cooling temperature, and holding time. Analysis of variance revealed that only pyrolysis temperature had a significant effect on biochar and pyrolysis liquid yields. The biochar and pyrolysis liquid yields fit by a second-order polynomial model agreed well with experimental results. As the pyrolysis temperature increased, the solid product yield decreased, while the pyrolysis liquid yield increased. The highest biochar and pyrolysis liquid yields were 56.11% and 38.53% that derive at 300 and 600 °C of pyrolysis temperature, respectively. The validation of both prediction models showed over 96% agreement. Biochar of high heating value (26.55 MJ/kg) was obtained at 600 °C pyrolysis temperature and 30 min holding time. According to the Van Krevelen plot, the molar ratios of the H/C and O/C of the biochar obtained at 600 °C of pyrolysis temperatures were similar to coal material. The high-quality biochar was of carbon storage class 4 according to the IBI classification; and the characteristics of pyrolysis liquid met community product standards of Thailand. An economic analysis was performed to assess the feasibility of converting 60 tons/year of durian peel into biochar and pyrolysis liquid. An internal project rate of return (IRR) of 25.91% with

a payback period of 1.58 years was estimated. The findings of this study indicate the economic viability of immediately deploying large-scale pyrolysis utilizing a waste stream from agriculture.

Keywords: Durian peel, Biochar, Pyrolysis liquid, Slow pyrolysis, Analytic Statistic, Economic analysis

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CHAPTER I

INTRODUCTION

1.1 Background and rationale

Durian is now becoming a popular and significant tropical fruit crop among farmers in Southeast Asia including Thailand (Siriphanich, 2011). According to the data from the Office of Agricultural Economics, in 2021, the overall durian plantation in Thailand is 138,478 hectares, with total durian production of 1,216,700 metric tons. Among them, approximately 50% of durian are produced from southern part of Thailand. These durians belong to the Bombacaceae family and genus *Durio*. The Chanthaburi Horticultural Research Center has been surveying and collecting cultivars in Thailand for more than 50 years (1967-present), with over 600 cultivars of *Durio zibethinus*, or indigenous durian (Chanthaburi Horticultural Research Center, 2019). Different species have unique flavor and odor profile. Durian peel is a type of biomass derived from agricultural residues, which are abundantly found in Thailand. Some common names of durian found in Southern Thailand are such as Monthong, Chanee, Kan Yao, Bacho, and Puangmanee (Horticultural Research Institute, 2020). In Thailand, durian cultivars are classified based on the leaf apex, leaf base, fruit shape, and fruit thorny shape, all of which are considered as very stable characteristics that do not fluctuate with environmental circumstances. This study used the durian peel, identified based on morphological categorization. In southern Thailand, three cultivars (PDP, MDP, BDP) of durians are highly popular for consumption and manufacturing.

In addition to household consumption of durian, there are also durian processing industries and entrepreneurs (registered business and community enterprises) which produce durian jam, fried durian chips, or frozen durian for domestic consumption or exported to foreign countries. The 60% by weight of durian consists of the peel (Purnomo et al., 2016), whereby many durian peels are just left

as waste from the durian processing. Durian peel has a strong odour and is difficult to naturally decomposed, thus it will cause unsanitary conditions if it is improperly disposed. Currently, durian peel is not utilized commercially, despite numerous studies on the potential uses such as antioxidant and anti-inflammatory activity (Chingsuwanrote et al., 2016), antimicrobial activity (Lipipun et al., 2002; O. Duazo, 2012), pectin (Maran, 2015), carboxymethyl cellulose (Rachtanapun et al., 2012; Suriyatem et al., 2019), flour (Charoenphun and Klangbud, 2019), charcoal briquettes (Nuriana et al., 2014), and paper (Masrol et al., 2015).

There are a few reports on durian peel processing by pyrolysis technology. Studies on the pyrolysis of durian peel indicate its potential utility in biofuel and biochemical production. Biochar can be used for adsorption, soil amendment, as a catalyst, etc. (Cha et al., 2016), while pyrolysis liquid has been used in organic agriculture, alternative medicine, food processing, etc. (Theapparatt et al., 2018). The fast pyrolysis of durian peel was studied with the effects of pyrolysis temperature (250-650 °C), the influences of the studied pyrolysis temperature ranges to the pyrolysis product yields were found. The temperature of 650 °C and a holding time of 10 min produced 23.51% biochar and 57.45% pyrolysis liquid. The yield of pyrolysis liquid was high because fast pyrolysis which normally operate at >20 °C/min heating rate tends to produce pyrolysis liquid maximally (Tan et al., 2017). Otherwise, slow pyrolysis using 1-10 °C /min heating rate is the best method for biochar production, resulting in a greater specific surface area of biochar and a 30–60% biochar yield (Li et al., 2020). Moreover, the investment cost of pyrolyzers and energy input for slow pyrolysis systems are lower than those for fast pyrolysis (Brown et al., 2011).

Recently, in the pyrolysis report using two feedstocks (Moso bamboo and heavy bio-oil (or light bio-oil) simultaneously, Response Surface Methodology (RSM) was chosen to assess the influences of the different experimental conditions (temperature, residence time (or holding time), and mass ratio) on the yield and quality of the products (Chen et al., 2022; Zhuang et al., 2023). The increasing mass ratio results in high biochar yield, while pyrolysis temperature and residence time showed an effect to decrease output (Chen et al., 2022). Similar to the liquid products, the

mass ratio has an effect while the resident time shows less influence. However, the pyrolysis temperature of this report shows an increased liquid yield at higher temperatures but a decreased product at temperatures exceeding 550 °C (Zhuang et al., 2023). Das and Goud (2021) utilized RSM to study the slow pyrolysis of rice husks. They investigated three parameters (pyrolysis temperature, nitrogen flowrate, and holding time); both pyrolysis temperature and holding time have significance with produced yield, in which the maximum achievable liquid yield of 35.2 wt.% with corresponding biochar yield of 48 wt.% was attained at 430 °C of pyrolysis temperature and 40 min of holding time (Das and Goud, 2021).

In pyrolysis processes, the operating parameters such as reactor type, biomass components, biomass particle size, heating rate, and reaction temperature affect the product yield distribution and quality (Li et al., 2020; Theapparath et al., 2019). Theoretically, increasing the pyrolysis temperature and holding time enhanced the decomposition of feedstock components, resulting in a higher liquid product but a decrease in solid yield, while their influences on the product characteristics are still uncertain. In addition, a lower cooling temperature can also result in a more efficient separation of pyrolysis liquid products. However, the investigation of an optimum cooling temperature is also needed for economic aspects. As per our best literature review, no reports have been published on the converting of durian peel to biochar and pyrolysis liquid by slow pyrolysis. Likewise, the effect of cooling temperature for liquid product recovery is still lack of information. The central composite design (CCD) was adopted for experimental design, and RSM was applied to explore the significance of the variables to both product yields. Comprehensive characterizations of biochar and pyrolysis liquid products were also compared to the product quality standards to assess the suitable future utilization and criteria for choosing the desired pyrolysis conditions. Moreover, the small industrial-scale plant for durian peel processing was designed, and its economic feasibility was also analyzed.

1.2 Review of Literature

1.2.1 Durian

The rise in durian production increases the quantity of durian waste. The durian content typically ranges between 20 and 25% by weight of durian seed and

75 to 80% by weight of durian peel (Lubis et al., 2018). Therefore, durian is one of the most economically significant fruits in Thailand. The scientific name for this plant is *Durio zibethinus Murray*, which belongs to the family of Bombacaceae. There are more than 30 kinds of durian. However, only nine are available for consumption: *D. zibethinus*, *D. dulcis*, *D. grandiflorus*, *D. graveolens*, *D. kutetensis*, *D. lowianus*, *D. macrantha*, *D. oxleyanus*, and *D. testudinarum* especially *D.zibethinus*, is a famous durian consumed all over the world (Pakkaew, 2016).

1.2.1.1 Composition of durian fruit

Typically, durian fruit is composed of 10-30% durian pulp, 50-60% peel, and 10-20% seeds (Fig. 1.1) (Purnomo et al., 2016).

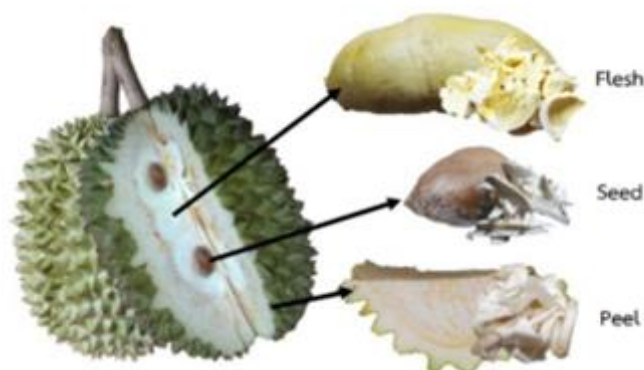


Fig. 1. 1 Morphological structure of durian fruit (Charoenphun and Klangbud, 2020)

Durian is rich in nutrition fruit; for example, durian pulp contains sugar, vitamin C, potassium, protein, carbohydrate, fat, vitamin B1, vitamin B2, vitamin E, phosphorus, calcium, iron, and a pungent smell (Ashari et al., 2015). Durian seeds contain between 50 – 70% carbohydrates (Mirhosseini et al., 2015), while durian peel includes 4.84 % ash, 13.09 % hemicellulose, and 15.45 % lignin (Jun et al., 2010). The chemical composition of durian fruit contains many carbohydrates and exists in the form of starch and sugar. Hemicellulose, an insoluble and indigestible polysaccharide carbohydrate, is also present in the digestive tract or dietary fiber. The sweetness of durian is mainly attributable to durian protein, and it will emit an odor when ripe. The physical transformation of durian from aging to impulse to maturity has occurred. Enzymes, a type of protein found in durian, are responsible for the sweetness experienced during starch transfer to sugar. Durian has

a 3.9% fat content; stearic and palmitic acids are durian's most abundant fatty acids. The durian is rich in vitamins and minerals essential for various body types. In addition, durian contains essential chemicals such as carotene (a fat-soluble pigment) and volatile molecules, such as thioether, esters, hydrogen sulfide, and diethyl disulfide, that give the fruit its distinctive odor (Pakkaew, 2016). The beneficial compounds in durian include antioxidants (Arancibia-Avila et al., 2008) and anti-inflammatory compounds (Chingsuwanrote et al., 2016).

1.2.1.2 Utilization of durian waste

During the season when durian products are put on the market, two-thirds of the durian fruit is consumed, causing much waste from durian fruit (Ong et al., 2011). Currently, there is research on using durian by-products and waste (Table 1.1) to be used in various fields of work.

Table 1. 1 Utilization of durian peel

Utilization	Results	Reference
Antioxidant and anti-inflammatory activities	The existing Monthong durian extract has better antioxidant and anti-inflammatory effects than Chundee durian extract.	(Chingsuwanrote et al., 2016)
Carboxymethyl cellulose	Carboxymethyl cellulose is prepared from cellulose extract of durian peel through carboxymethyl. The addition of glycerol increases the flexibility of the film, while the young's modulus decreases. On the other hand, by adding PEG-10 Dimethicone, the flexibility of the film decreases.	(Khemkaew, S. and Kaewpirom, 2016)
Flour	As durian substitutes increase, the firmness of gluten-free pasta increases.	(Charoenphun and Kwanhian, 2020)
Charcoal briquette	The result of the thermal efficiency analysis concluded that the charcoal briquette of durian peel produced by this community has 6,134 calories per gram, which is higher than the standard and produces 6.2% ashes. Its performance complies with community product standards.	(Chutsawang, 2013)
Paper	Two types of durian peel paper for inkjet printing were studied. The ratio of durian thin pulp to Saa pulp is 75% to 25% (O/D weight), so that the paper has the best physical properties.	(Tipsotnaiyana N. and Netpradit S., 2007)

Furthermore, extract important biologically active substances, such as antioxidant activity, anti-inflammatory, inhibit pathogenic microorganisms, develop polysaccharide gel from durian peel to eliminate oral peritonitis, extract hydrocolloids (such as gums) and use it as emulsifiers for food, pectin and carboxymethyl cellulose for the production of edible coatings and biofilms, use immature durian, seeds, and peels to produce starch for the production of gluten-free pasta, including charcoal briquette production, paper strips, and other fields.

1.2.2 Pyrolysis system

1.2.2.1 Fundamental principles of pyrolysis

Lignocellulosic biomass by thermal decomposition with the pyrolysis process occurs in an inert atmosphere without oxygen. The primary reaction of the chemical is highly complicated and contains various steps. The final pyrolysis yields from biomass include biochar, pyrolysis liquid, and syngas. The process of pyrolysis mainly spits out carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and hydrogen (H_2). The organic substance in the biomass precursor appears to decay approximately 350–550 °C and handle up to 700–800 °C, unavailable of air/oxygen (Atsonios et al., 2015). The macromolecules of the organic material begin to degrade to produce small molecules, excused into the gas, condensed vapor (tar and oil), and solid charcoal by the process stream during the process of pyrolysis. The amount of each final yield is conditioned on heating rate, holding time, pressure and temperature, the type of reactants, and the configuration and design of the reactor. Fig.1.2 shows the degradation system of residues of lignocellulosic at several temperatures.

Biomass moisture matter is likewise an essential part of the pyrolysis process. During the rapid pyrolysis process, the moisture content of the raw materials should be about 10% (Bridgwater et al., 1999). Due to high humidity, the main product becomes liquid, and if the water level is low, the risk of a process that generates much dust instead of oil is high. Therefore, the sludge obtained from waste streams and meat processing waste streams must be dried before exposure to the pyrolysis environment. Below 450 °C, at which slow heating rate, the primary output is biochar. Though, at a temperature higher than 800 °C, with a higher heating rate, more gaseous and ash yields will be produced. Pyrolysis liquid can be produced at relatively high heating

rates at moderate temperatures. At the beginning of the process, at 250-300°C, the release rate of volatile substances is 10 times faster than the next step (Lanzetta and Di Blasi, 1998).

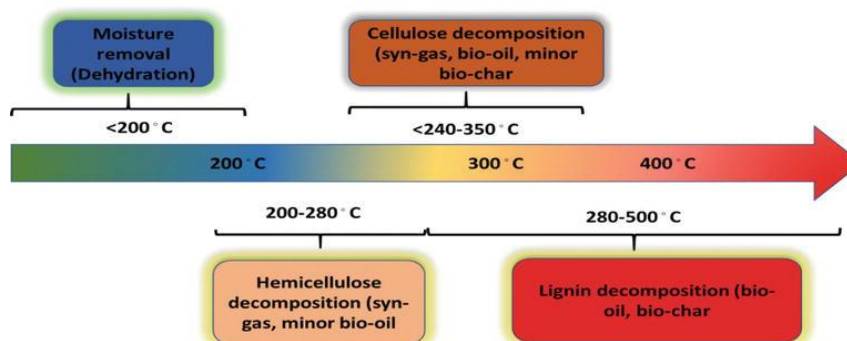


Fig. 1. 2 The decomposition at different temperatures of biomass

Normally, wood biomass is used in charcoal production. Charcoal in heating manufactured derived a small smoke quantity in the past, widely consumed to melt ore to separate iron. However, this method has disadvantages: low yield, excessive air pollution, and low energy. Since then, modern technologies have been established to draw biomass with the greatest energy using gasification, pyrolysis, and combustion (Faravelli et al., 2010). Combustion involves biomass burning in oxygen presence to produce heat. The abilities of this system are not suitable (Pei-dong et al., 2007; Thornley et al., 2009). Gasification also occurs in an oxidizing atmosphere that provides gas fuel. However, pyrolysis is the main stage of combustion and gasification (Fisher et al., 2002). Therefore, pyrolysis can be considered part of combustion and gasification (Grønli et al., 2002). The decomposition products of biomass during pyrolysis are shown in Fig. 1.3 (International Energy Agency, 2006).

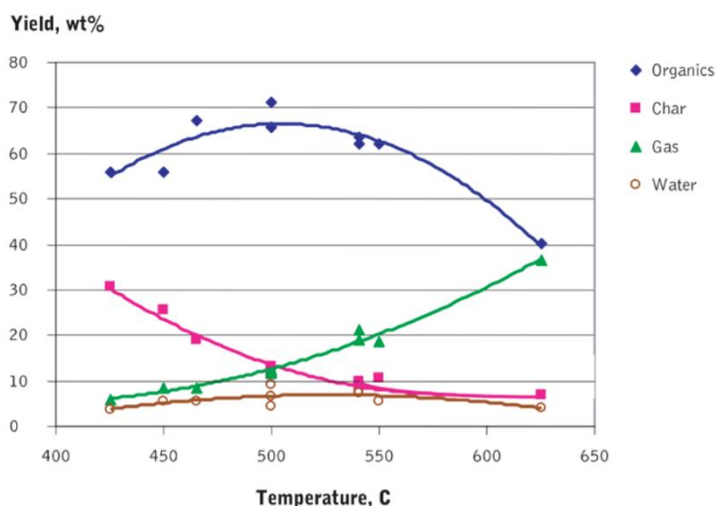


Fig. 1.3 The pyrolysis product of the decomposition of biomass

Table 1.2 Review the list of major pyrolysis interactions at different temperatures (Jahirul et al., 2012)

Temperature	Reaction type	Final products
Less than 350°C	Depolymerization, moisture loss, free radical generation	CO and CO ₂ gas liberation, carbonyl and carboxyl group production, biochar formation
During 350-450°C	Substitution for breaking of glycoside chain of polysaccharide	Tar production containing levoglucosan, anhydrides and oligosaccharides
Above 450°C	Dehydration, rearrangement, and fission of sugar units	Acetaldehyde, glyoxalin and acrolein production
Above 500°C	A mixture of all above processes	A mixture of all above products
Condensation	Unsaturated products condense and cleave to the char	A highly reactive char residue containing trapped free radicals

1.2.2.2 Classification of pyrolysis methods

There are three types of pyrolysis are conventional/slow pyrolysis, fast pyrolysis, and ultra-fast/fast pyrolysis. Table 1.3 summarizes each method differences in temperature, holding time, heating rate and products yield. As mentioned before,

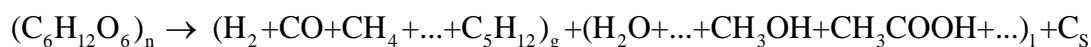
slow pyrolysis is often used to modify solid materials to reduce the amount of liquid produced. Fast pyrolysis and ultra-fast pyrolysis (flash) can maximize the production of gas and liquid (Lewandowski et al., 2020).

Table 1.3 Classification of pyrolysis methods

Method	Temperature (°C)	Holding Time	Heating rate (°C/s)	Major products
Slow pyrolysis	400-500	5-30 min	10	Solid
Fast pyrolysis	400-650	0.5-2 s	100	Liquid, gas
Flash pyrolysis	700-1000	<0.5 s	>500	Gas

1.2.2.3 Pyrolysis process

As shown in the equation, pyrolysis is the thermal decomposition process of biomass or other raw materials in an anaerobic state.



There are two main types of pyrolysis: slow pyrolysis and fast pyrolysis. Slow pyrolysis is the conversion of biomass over a prolonged heating period. It uses a lower heating rate, the main product is biochar (>30%), and fast pyrolysis is used to convert biomass in a shorter holding time. The main product with a rapid heating rate is bio-oil or pyrolysis liquid (>50%) (Qambrani et al., 2017).

1.2.2.4 Factors affecting pyrolysis

1) Biomass type

As reported by (Akhtar and Saidina Amin, 2012), each type of biomass contains different amounts of lignocellulose, which affects the product yield during the pyrolysis process. Cellulose and hemicellulose are responsible components of pyrolysis liquid, while the lignin constituent of the product is biochar.

2) Biomass pretreatment

Generally, the biomass entering the pyrolysis process must be pretreated to reduce its size and change or destroy the structure of the lignocellulose components, which will affect the product yield after pyrolysis. Biomass pretreatment technologies are mainly divided into five categories:

- Physical, such as milling and pressing, etc.
- Thermal, such as steam explosions and torrefaction, etc.

- Chemical, such as pretreatment with acids, alkalis, and ionic liquids, etc.

- Biological, such as using enzymes, etc.

- Co-pretreatment (Mohan et al., 2006)

3) Temperature

The pyrolysis temperature has a significant influence on the performance and yield of the product. The liquid yield is highest at a temperature of 400 to 550 °C and above 600 °C. Due to the secondary reaction, the products of liquid and char are converted into a gas (Mohan et al., 2006).

4) Heating rate

The heating rate is a parameter that characterizes the type of pyrolysis. The rate of fast pyrolysis is the high heating rate, while the low heating rate is slow pyrolysis (Mohan et al., 2006). A high heating rate leads to rapid degradation of the biomass structure, resulting in a higher gas yield than a solid yield. In contrast, a low heating rate slows the decomposition of the biomass structure, showing more solid products than gases are produced. Therefore, the heating rate influences the yield of pyrolysis products.

5) Holding time

A shorter reaction time is effective for liquid products because VOCs are released at the beginning of the reaction, and the reaction time does not directly affect the yield of the product. On the contrary, it directly affects the quality of the product obtained by pyrolysis.

The pyrolysis process can be adjusted by controlling various process factors to achieve the most specific product state (Chen and Lin, 2016). Slow pyrolysis uses a temperature of 350-700 °C. Those produce the highest solids or biochar. Setter et al. (2020)(Setter et al., 2020) studied the production of biochar from coffee husk briquettes through slow pyrolysis shown that the maximum biochar is 39.82% at 350 °C. Like Ghysels et al. (2020)(Ghysels et al., 2020) study, cocoa pods can be slow pyrolysis at a temperature of 350 to 500 °C, with a maximum biochar yield of 48%. The utilization of biomass to produce biochar and pyrolysis liquid pyrolysis has been widely used in recent years. However, most biomass to produce biochar and pyrolysis liquid is hardwood.

In addition, no more research has been conducted on using durian peel to produce biochar and pyrolysis liquid. There may be numerous factors involved in biochar production. The other pyrolysis research conditions are shown in Table 1.4.

Table 1. 4 Summarize research conditions for pyrolysis and yield

Biomass	Pyrolysis conditions	Result	References
Coconut shell	Sample: Moisture 7.82%, Quantity 4 g, Size 250 μm , HHV 9.62 MJ/kg Condition: Ar flow 100 mL/min, Heating rate 10 $^{\circ}\text{C}/\text{min}$, Temp. 400-800 $^{\circ}\text{C}$	Maximum yield Biochar 33.6% at 400 $^{\circ}\text{C}$ Pyrolysis liquid 48.7% at 600 $^{\circ}\text{C}$ Syngas 18.34% at 600 $^{\circ}\text{C}$	(Sarkar and Wang, 2020)
Malt bagase	Sample: Moisture 2.24%, Quantity 40 g, Size 0.5 mm, HHV 18.16 MJ/kg Condition: N_2 flow 150 mL/min, Heating rate 5 $^{\circ}\text{C}/\text{min}$, Temp. 500, 600, and 700 $^{\circ}\text{C}$, Holding time 10, 30 and 50 min	Maximum yield Biochar 29.71% at 500 $^{\circ}\text{C}$ Pyrolysis liquid 47.67% at 700 $^{\circ}\text{C}$ Syngas 36.40% at 500 $^{\circ}\text{C}$	(Machado et al., 2020)
Poplar wood	Sample: Quantity 5 g, Size 50 μm Condition: N_2 flow 100 mL/min, Temp. 100-800 $^{\circ}\text{C}$, Holding time 30 min	Maximum yield Biochar 35.7% at 350 $^{\circ}\text{C}$ Pyrolysis liquid 21.1% at 500 $^{\circ}\text{C}$ Syngas 65.08% at 800 $^{\circ}\text{C}$	(Zhang et al., 2020)
Coffee husk briquette	Sample: Moisture 9 %, Quantity 1.5 kg, Size 7 \times 10 cm, HHV 15-20 MJ/kg Condition:	Maximum yield Biochar 39.82% at 350 $^{\circ}\text{C}$	(Setter et al., 2020)

Biomass	Pyrolysis conditions	Result	References
	Heating rate 5 °C/min, Temp. 350, 400, and 450 °C, Holding time 30 min	Pyrolysis liquid 33.59% at 400 °C Syngas 31.94% at 450 °C	
Cotton stalks	Sample: Moisture 8.6%, Quantity 20 g, Size 1-3 mm, HHV 18.32 MJ/kg Condition: N ₂ flow 0.5 L/min, Temp. 300-800 °C, Holding time 30 min	Maximum yield Biochar 86.5% at 300 °C Pyrolysis liquid 32.88% at 800 °C Syngas 39.12% at 800 °C	(Al Afif et al., 2020)

1.2.3 Biochar

The application of biochar is different from charcoal. Ordinary charcoal refers to its use as fuel, while biochar is used to store carbon in the soil and improve the physical condition of the soil. Due to the characteristics of biochar, when inserted into the soil, it is naturally porous, supporting to ventilate, penetrating, absorbing, and retaining nutrients. It is the existence of microorganisms that reduce the acidity of the soil. It also improves the quality of the fertilizer, thereby saving fertilizer use, reducing costs, increasing income, and improving productivity, a technology that farmers, families, communities can develop, and local organizations (Spokas et al., 2012). Furthermore, the structural feature with many areas, which is characterized by negative ions on the contact surface, helps increase the cation exchange capacity (CEC) of positively charged nutrients. Therefore, it is also a way to accumulate nutrients for plants and has the characteristics of biochar with a substantial alkalinity value (pH), especially for degraded soils and long-term accumulation of chemicals (Liang et al., 2006).

1.2.3.1 Conditions of pyrolysis

Biochar is a product from pyrolysis that includes all the non-combustible components of the raw material. Consequently, irrespective of the process temperature and raw material, biochar never occurs as a pyrolysis and

gasification product. The use of slow pyrolysis technology can maximize the production of biochar. On the other hand, under fast pyrolysis conditions at high temperatures, biochar production will decrease. In contrast, in slow pyrolysis at a temperature of 300-700 °C, the heating rate is 1-100°C/sec, and the pyrolysis time is several minutes to several days (Cantrell et al., 2012; Qambrani et al., 2017; Spokas et al., 2012). For biochar analysis from an individual material type, pyrolysis temperature, holding time, and oxygen exposure will affect the quality and quantity of biochar produced.

1.2.3.2 Yield and fixed carbon content

Generally, the maximum increase of pyrolysis temperature leads to decreases yield (by weight) and carbon content (by weight) of the biochar with the release of increased hydrogen, nitrogen, and oxygen in the raw material through the gas phase (Mašek et al., 2013). The slow pyrolysis system usually produces 35% of biochar (by mass, the proportion of dry raw material converted into biochar). The typical fast pyrolysis system can produce 12% of biochar (Qambrani et al., 2017). Despite this tendency, current reports contain established that produce pyrolysis at low and high temperatures similar to stable carbon. This is because more stable carbon products (lower quantity) are achieved during pyrolysis at high temperatures, and the carbon content is low (higher quantity) products achieved at low-temperature of the pyrolysis process (Mašek et al., 2013).

These results indicate little difference from the perspective of pyrolysis biochar at low-temperature and high temperature (Mašek et al., 2013), as can be observed from Table 1.5, which significantly mentions that the carbon amount of biochar depends on the raw materials chosen.

Table 1. 5 The properties of biochar produced by pyrolysis, related raw materials and pyrolysis conditions

Feedstock	% Moisture	Pyrolysis temp. (°C)	Biochar yield (%wt.)	Stable carbon yield (%)	Surface area (m ² /g)	pH	Reference
Corn Cob	11.7	300	77.3	49.1	61.8	8.1	(Liu et al., 2014)
		400	36.9	71.7	180.1	9.1	
		500	23.3	81.6	212.6	9.3	
		600	21.7	82.4	192.9	10.4	

Mixed larch and spruce wood chips	30	350	44 (est.)	72 (est.)			(Mašek et al., 2013)
		450	36 (est.)	78 (est.)			
		550	30 (est.)	86 (est.)			
Peanut Shells	Air dried, n/a	400	40	59	0.52	7.9	(Novak et al., 2009)
		500	35	56	1.22	8.6	
Softwood Pellets	6	350	38 (est.)	72 (est.)			(Mašek et al., 2013)
		450	31 (est.)	78 (est.)			
		550	28 (est.)	84 (est.)			
Soybean Stover	Dried, % n/a	300	37.03	68.81	5.61	7.27	(Ahmad et al., 2012)
		700	21.59	81.98	420.3	11.32	

1.2.3.3 Utilizations of biochar

The current use and application of biochar could be a profoundly active field of investigation with an ongoing search about comes. Underneath is a few everyday uses of biochar, as backed by current literature.

1) Substitution of activated carbon

The high content of carbon (65-90%) in biochar and the high surface area caused by micropores are two primary characteristics that can give activated carbon excellent applications in filtration/refining, chemical reactions, and adsorption (Azargohar and Dalai, 2006). Therefore, the identity of activated carbon and biochar has led to many studies on using biochar instead of activated carbon. The specific surface area of activated carbon is 500-1600 m²/g so that it can be used in advance. The surface area characteristics of biochar produced by low-temperature pyrolysis are lowest during 0.7-13.6 m²/g, as the surface area characteristics of biochar produced by high-temperature pyrolysis are up to 460 m²/g that highest (Qambrani et al., 2017).

2) Control of odor

Similar to activated carbon, biochar is often used due to the control of odor ability. Air molecules adsorption has been studied that causes fecal odors. The biochar materials obtained from bamboo, human feces, pine, and wood were equally effective and with activated carbon controls for efficacy to absorb odors. While fecal odors cannot be eliminated 100%.

3) Amendment of soil

Although many studies have analyzed the impact of soil biochar and crop yield, there are still differences. In terms of crop yields, a meta-analysis was performed by Jeffery et al. (2011). It was established in all studies as fourteen samplings, which was a negligible positive, statistically significant progressive influence on crop yields, and crop efficiency increased by 10%. Although crop yields vary widely (-28 to +39%), the best improvement usually observed in biochar is in acidic or neutral pH soils and medium/gravelly soils (Jeffery et al., 2011). Added biochar with 100 tons/hectare showed the most significant enhancement in crop yield with +39% (Jeffery et al., 2011), which is critical to observe that another report also recorded a +64% increase in crop yield (Hossain et al., 2010), a 146% increase in crop yield (Peng et al., 2011), and a 250% increase in crop yield (Van Zwieten et al., 2010), while the addition of biochar usually brings the most significant improvement except fertilizers, only slight enhancements are observed (Hossain et al., 2010; Peng et al., 2011; Van Zwieten et al., 2010). Although the products are the most widespread, research shows that adding biological agents to soil able to enhance the water retention capacity of the soil (Ding et al., 2010; Karhu et al., 2011; Peng et al., 2011), retention of nutrients (Ding et al., 2010), pH (may replace agricultural lime) (Galinato et al., 2011; Novak et al., 2009; Peng et al., 2011), organisms of soil (Atkinson et al., 2010; Solaiman et al., 2010; Warnock et al., 2010) and exchange capacity of cation (Peng et al., 2011; Van Zwieten et al., 2010), as reducing emissions in the soil (Karhu et al., 2011). Nevertheless, that identified that the temperature of pyrolysis, time of pyrolysis, beginning raw materials, increased biochar content, and primary composition of chemicals in the soil affect the biochar capacity of the soil and have a positive impact on the yield of soil and crops. In addition, total the earlier-mentioned investigations were carried out at one time of several months to two years, and there still needs to be long-term research on the biochar effects on soil (Jeffery et al., 2011).

4) Waste management of solid

The similarity of biochar and activated carbon has prompted the study of the application of biochar using traditional waste management systems. In large-scale landfill operations, it was archived that biochar helps restore leachate and reduces the impact of the landfill on the environment. At the same time, minor composting treatment is carried out to manage organic solid waste (Qambrani et al., 2017).

1.2.3.4 Reduction of greenhouse gas emission

1) Stability of carbon

The carbon sequestration potential of biochar comes from the stability of carbon, which can prevent the carbon contained in biochar from degrading into lighter hydrocarbons in the short term, as well as by gas emissions-greenhouses such as CO₂ or CH₄ into the atmosphere. Individual biochar can retain its configuration (carbon stability is higher) and, to return, prevent carbon into the atmosphere; very interested in biochar in carbon sequestration plans. Generally, the stability of carbon in biochar was evaluated by concluding the half-life or retention time of that average of carbon in the biochar. Mention of half-life, that time at which medium the available carbon at initial on biochar has decreased (like the moderate), that average retention time mentions it takes for carbon into the soil to be transmitted to the environment (like average) (Woolley and Hallowell, 2018). Singh et al. (2012) a five-year laboratory study was conducted to demonstrate how the carbon stability of biochar changes with raw materials (eucalyptus and leaves, sludge from paper mills, poultry waste, cow dung) and pyrolysis conditions. Researchers used the carbon-13 test for the biochar stability and established that the biochar during 0.5-8.9% was mineralized in the five-year study lesson (Singh et al., 2012). They established that, depending on the raw material and pyrolysis conditions, the average residence time of biochar is 90-1600 years; see Table 1.6 below. Biochar from manure, raw materials, and biochar produced at pyrolysis at low temperatures have low carbon stability (Singh et al., 2012).

Table 1. 6 Biochar carbon stability

Raw material	Temperature (°C)	Steam activation	Average residence time of carbon (years)
Eucalyptus saligna wood	400	Yes	326
Eucalyptus saligna wood	400	No	294
Eucalyptus saligna wood	550	Yes	1271
Eucalyptus saligna wood	550	No	1616
Eucalyptus saligna leaves	400	Yes	270
Eucalyptus saligna leaves	550	Yes	572
Paper mill sludge	550	Yes	102
Poultry litter	400	No	129
Poultry litter	550	Yes	396
Cow manure	400	No	90
Cow manure	550	Yes	313

2) Sequestration of carbon

One of the recommended results to address the continuous rise in the concentration of CO₂ in the atmosphere and the level of human CO₂ emissions is to achieve carbon sequestration through biochar preparation. Many biochar scientists and supporters have proposed that when the process of biochar production is optimized, biochar yield can offset 12% (or about 1.8 PgCO₂-C; (Woolf et al., 2010)) when the operation has increased efficiency for the production of bio-energy, the annual output can reach up to 10%, which is better than other carbon sequestration technologies used today.

1.2.4 pyrolysis liquid

1.2.4.1 Characterization of pyrolysis liquid

1) Physicochemical properties of pyrolysis liquid

Pyrolysis liquid has a smoky smell with a light yellow to dark brown, as shown in Fig.1.4, which varies based on biomass usage. Smell mixtures, including derivatives of ester, ketones, furan and pyran, nitrogen, and phenol, provide the smell of pyrolysis liquid (Guillén and Manzanos, 2005). Alkyl guaiacol derivatives (sweet, smoky, woody), alkyl phenol derivatives (cresols and pungent flavor), alkyl syringol derivatives (light, heavy, burnt), guaiacol (smoky sweet, pungent), phenolic compounds are phenols (pungent), and syringol (smoke)

contributes to the odor and taste of pyrolysis liquid (Kim et al., 1974).



Fig. 1. 4 Bottles of non-distilled (left) and distilled (right) mangrove pyrolysis liquid
(Chan et al., 2012)

Pyrolysis liquid from birch without bark heartwood contains water at 74.7% and organic matter at 25.3% (Hagner, 2013). The viscosity of pyrolysis liquid in *C.oleifera* is 1.08 cSt, and the content of moisture is 84% (Xu et al., 2013), and (Rakmai, 2009) research that pyrolysis liquid samples in white popinac, bamboo, rubber wood, and eucalyptus contained 78–88% water. According to reports, rubber wood boiling point is 96–108 °C (Ratanapisit et al., 2009). Table 1.7 lists the physicochemical properties and yields of pyrolysis liquid from different plant sources.

Table 1. 7 Physicochemical properties of pyrolysis liquid from different plants

Biomass	pH	Density	Organic acid content (%)	Yield (%)	References
Rubber wood	2.90-3.80	1.009-1.027	-	23-29	(Ratanapisit et al., 2009)
Birch heartwood	1.80-2.90	-	-	38-43 (including tar)	(Fagernäs et al., 2012)
Walnuts tree branches					(Wei et al., 2010a)
WP1	3.49	1.034	2.73	11.4	
WP2	3.32	1.050	3.01	31.4	

WP3	2.76	1.072	3.12	1.45	
Moso bamboo	2.50	1.090	3.80	-	(Lin and Shiah, 2006)
Walnuts shell					(Wei et al., 2010b)
SP1	3.02	1.013	6.31	-	
SP2	2.98	1.045	2.85		
SP3	3.32	1.035	2.07		
Eucalyptus	-	-	-	45.5	(Souza et al., 2012)
Mixed chips of Quercus sp.	<2.50	-	4.6-5.5	-	(Choi et al., 2012)
Camellia oleifera shell	3.50	-	-	30	(Xu et al., 2013)
Rosemary leaves					(Ma et al., 2013)
Fresh	-	-	-	65	
Air dried	-			25	
Coconut shell	2.90	1.020	-	-	(Wititsiri, 2011)

2) The chemical properties and composition of pyrolysis liquid

Slow pyrolysis usually produces in crude distillation, which separates it into a liquid stage called pyrolysis liquid, while the dark, non-fatty ground phase is called scorched pyroligneous tar (Amen-Chen et al., 1997; Fagernäs et al., 2012; Souza et al., 2012). Pyrolysis liquid storage below 300 °C will produce fewer effective compounds. This is because hemicellulose degraded and cellulose degraded during this period. However, storing pyrolysis liquid at temperatures above 425 °C will cause the tar to decompose. The carcinogens are 3,4-Benzopyrene and 1,2,5,6-Dibenzanthra-Cenementryl Cholnisrene, although these substances can be eliminated. It is easy to re-distill at 60-70 °C, but re-distillation loses some agriculturally

beneficial compounds (Phisatan et al., 2015). The distillate ratio is based on raw material, procedure, and conditions of storage (Rakmai, 2009). Because PAHs exist, it can be challenging to use tars for purposes other than energy. However, a wood preservative can be used (Fagernäs et al., 2012). The pyrolytic composition acid changes according to the temperature, heating rate, and raw material properties through pyrolysis.

Usually, pyrolysis liquid has a complex mixed composition of acetic acid, carboxaldehyde, catechol, carboxylic acids, furans, guaiacol, hydroxy ketones, isoeugenol, methanol, phenol, pyrans, sugars, syringol, vanillin, and other (Berahim et al., 2011; Guillén and Manzanos, 2005). The pyrolysis liquid that extracts dichloromethane from the pineapple plant's waste biomass contains many phenolic compounds, especially 1,2-benzenediol (catechol), 2,6-dimethoxy phenol, 3-methoxy 1,2-benzenediol and phenol. Alkyl aryl ether (9.33%), ketone (7.76%), and phenol (69.5%) in the pineapple waste biomass were identified as critical constituents of pyrolysis liquid, consisting of the pineapple leaves and the remaining stems in the field after harvesting that derivatives of furan and pyran (3.57%), sugar (2.85%), acid (2.67%), ester (1.81%), aldehyde (1.05%), alcohol (0.9 %) and derivatives of nitrogen (0.14%) are secondary elements (Mathew et al., 2015).

3) Potential derivations of chemical components in pyrolysis liquid

The components in pyrolysis liquid can examine back to the lignocellulosic spine in the cell wall of plants. The lactones and furans are constructed in pyrolysis liquid mainly by hemicellulose hydrolysis. Phenolic acids and ketones are listed with significant results of xylan pyrolysis. This contains many cyclopentenones and 1-hydroxy-2-propanone with ethyl and methyl substituents and basic phenols with methyl substituents. Moreover, acetic acid, propionic acid, and a small amount formed of aromatics (Stefanidis et al., 2014). The xylose unit in hemicellulose degraded to an acetyl group that occurs high acetic acid in pyrolysis liquid. In addition, xylan degradation produces 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, 2-furfuraldehyde, acetic acid, methanol, propionic acid, and water. The methyl ester decomposition occurs high methanol or ether produced by the decomposition of the methoxy group of uronic acid and pectin-like plant substances

(Demirbas and Arin, 2002), that the breakage of the ferulate substituents on xylan, in particular probably originate to phenols and the gas stage unsaturated polymerization light materials (Evans and Milne, 1987).

Contrastingly, the degradation of cellulose will release dehydrated 1,4:3,6-dianhydro- α -D-pyran glucopyranose and levoglucosan (1,6-anhydro- β -D-glucopyranose) (Stefanidis et al., 2014). In pyrolysis conditions with a temperature higher than 300 °C, cellulose is converted to glucose, and levoglucosan is formed by removed water molecules (Balat et al., 2009). Major pyrolysis of cellulose achieved 1,4:3,6-Dianhydro- α -d-glucopyranose or levoglucosan by minor pyrolysis (Kawamoto et al., 2007). Basic aldehydes, cyclic ketones, phenols, and a small amount of alcohol were detected from the pyrolysis of cellulose (Stefanidis et al., 2014).

Compounds of smoky odor, such as 4-methyl guaiacol, eugenol, guaiacol, and phenol, are the product of lignin thermal degradation (Balat et al., 2009). The lignin thermal decomposition causes the breakage of the weak α -ether and β -ether bonds in the lignin structure, releasing guaiacyl and syringyl aromatic compounds. These aromatic compounds continue to form catechol and pyrogallol through the homogenization reaction of the O-CH₃ bond, or kind cresol and xylenol through the rearrangement reaction induced by free radicals (Asmadi et al., 2011a). Additionally the cresol degradation through demethylation produces phenol (Asmadi et al., 2011b).

1.2.4.2 Utilizations of pyrolysis liquid

1) The organic agriculture

Using chemical fertilizers will not only cause a heavy burden and pollution to the environment but also threaten our health. Long-term use of chemical fertilizers can cause the following problems: exhaustion of soil organic matter, reduction of water and nutrients, deterioration of soil structure, and water and heavy soil losses. Not only adding too much chemical fertilizer but also polluting the soil, water, and air and retaining most of the residues in vegetables, which reduces the quality and safety of our food supply. Therefore, finding and developing natural materials for vegetable production is significant. Pyrolysis liquid is ideal for organic farming because pyrolysis liquid is a natural organic compound. Many toxic

chemicals in agriculture have been replaced by pyrolysis liquid, which is a natural product that has been used to promote the growth and productivity of crops such as rice (*Oriza Sativa*) (Son et al., 2003), sweet potato (*Ipomoea batatas*) (Hua et al., 1998), sugar cane (*Saccharum officinarum*) melon (*Cucumis melon*) (Hua et al., 1998). It can also be used to improve fruit quality, resist diseases and insect pests, accelerate seed germination, and as a herbicide (Hua et al., 1998).

2) Alternative medicine

It is believed that pyrolysis liquid can improve body balance and recovery. Toxins can accumulate in the body from various sources, such as polluted air and, as a by-product of our metabolism, chemical pesticide and fertilizers from food. The continued accumulation of toxins results in poor health manifested by weakness, disease and sickness, pains and aches.

Pyrolysis liquid is a prebiotic and is defined as an indigestible food ingredient that positively affects the host by stimulating the growth and activity of one or a limited number of bacteria in the colon so it can improve the health of the host. Consuming less fiber, more meat and carbohydrates, and toxins can reduce the beneficial bacteria in the colon. Pyrolysis liquid is a source of short-chain fatty acids, which can promote acidity in the colon, thereby inhibiting the growth of harmful bacteria, enteropathogenic bacteria (Nakai and Siebert, 2003) and protozoa, *Cryptosporidium parvum* (Kniel et al., 2003) also stimulate the growth of prebiotics, *Enterococcus faecium* and *Bifidobacterium thermophilum* (Watarai and Tana, 2005). It also reduces the absorption of alkaline carcinogens, improves the absorption of calcium and magnesium, and improves blood circulation.

3) Food processing

Food is affected by many environmental conditions, such as temperature changes, oxidation, and exposure to microbes that may change the original composition. Since food is easily contaminated during manufacturing, processing and storage, it can also cause diseases. Food-borne diseases are underreported, and for millions of people worldwide, this is usually a common and sometimes fatal problem (Vattem et al., 2004).

Food additives play an important role in maintaining the quality and characteristics of food that consumers demand to retain food safety. They can be

classified according to one of their six main functions: preservation, nutritional enhancement, adding or changing colors, filling or changing flavors, and improving texture (Branen, 2002). Due to increased consumer awareness, the worldwide demand for synthetic food additives is declining. Therefore, natural food additives are very popular (Deba et al., 2008). Many natural additives and preservatives are widely used in foods, such as spices, herbs, essential oils, and pyrolysis liquid.

1.3 Objective of research

- 1) To investigate the thermal and chemical properties of three indigenous durian peels, namely Monthong (MDP), Puangmanee (PDP), and Bacho (BDP)
- 2) To investigate the effect of pyrolysis temperature, cooling temperature for liquid product recovery and holding time on the production yield of biochar and pyrolysis liquid from MDP using slow pyrolysis technology.
- 3) To evaluate the economic assessment of the biochar and pyrolysis liquid production from durian peel in large scale.

CHAPTER II

RESEARCH METHODOLOGY

2.1 Method

Slow pyrolysis was used in this study to obtain biochar and pyrolysis liquid, and a schematic diagram is shown in Fig. 2.1. The slow pyrolysis reactions were carried out in a vertical, tubular, stainless steel reactor (4 cm inside diameter \times 60 cm high), which was heated by an electric furnace. First, 100 g of dried ground durian peel was placed into the sample tube, then heated at 5 °C/min heating rate and held at the set pyrolysis temperature of 300, 450 or 600 °C for the set holding time after the desired temperature was reached for 30, 60 or 90 min. The system was operated under continuous nitrogen (purity-99%) flushing at 50 mL/min (velocity 6.63×10^{-4} m/s). To condense the vaporized pyrolysis products, the sample tube was connected to two condensers (Liebig, 2.7 mm inside diameter \times 40 cm total length) insulated with 13 mm thick EPDM (ethylene propylene diene monomer) closed cell elastomeric thermal insulation. Water mixed with ethylene glycol was used as the collecting media, with condensation temperature set at -5, 10 or 25°C during the process. The condensed pyrolysis liquid was collected in a glass bottle next to the condenser. At the same time, the biochar left in the sample tube was collected at the end of the pyrolysis after the system was cooled at room temperature. The collected pyrolysis liquid and biochar were weighted and characterized as described in the next section.

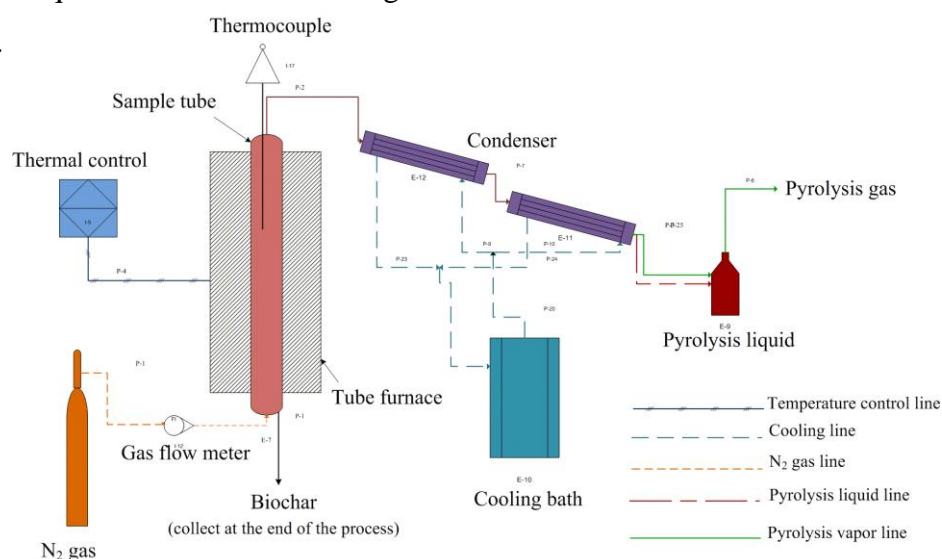





Fig. 2. 1 Schematic diagram of the pyrolysis system

2.2 Material and Equipment

2.2.1 Sample preparation

The durian peels used in this study consist of three types of indigenous durian peel namely Monthong (MDP), Puangmanee (PDP), and Bacho (BDP) which were collected from the local market in Pattani province, Thailand. The samples were initially cut into small pieces, dried at temperature 105 °C for 8-12 hour, crushed, and sieved to an average size within the range of 850 μm -2.00 mm for further pyrolysis process and with the size of <850 μm for further characterization.

Table 2.1 Types of durian fruit and thorny shapes

Durian type	Picture	Fruit shapes	Thorny shapes
PDP		Oval	Pointed-convex
MDP		Oblong	Pointed
BDP		Elliptic	Concave

2.2.2 Characterization method

2.2.2.1 Proximate analysis

The proximate analysis including moisture content, volatile matter, fixed carbon and ash content for all durian peel and biochar samples were determined according to ASTM D7582 by using a LECO TGA701 Macro Thermogravimetric Analyzer (TGA). For each run, a crucible containing 1 ± 0.1 g of the sample was carefully measured and placed inside the furnace zone of the macro TGA. Then weighed test specimens were then heated in crucibles without the covers from 25 to

107°C at 6°C/min until constant mass was reached (the weight loss is moisture content). The crucibles were then covered and the furnace temperature was raised from 107°C to 950°C at 50°C/min and kept for 7 minutes (the weight loss is volatile matter). Later, the furnace was cooled from 950 to 600°C. Then, the crucible covers were removed together and changing the furnace atmosphere to oxygen or air before heating again from 600 to 750°C at 3°C/min until constant mass (about 2 hours) for ash determinations (the weight of remained residue is ash) was obtained. Fixed carbon can be calculated by using the following equation (2.1).

$$\text{FC (wt. \%)} = 100 - (\text{MC} + \text{VM} + \text{AC}) \text{ (wt. \%)} \quad (2.1)$$

where FC is fixed carbon, MC is moisture content, VM is volatile matter and AC is ash content.

2.2.2.2 Ultimate analysis

The ultimate analysis was conducted using a CHNS/O analyzer, Flash 2000, Thermo-Scientific, to quantify the carbon, hydrogen, nitrogen, sulfur, and oxygen, with a higher and lower heating value, in three durian peel and biochar samples. The CHNS/O analyzer examines the elements of C, H, N, S, and O in samples by burning them at a high temperature into a mixed gas separating the quartz reactor between CHNS and O elements. Then, the gas mixture was separated in the column to measure the gas composition and converted to the elemental composition in the durian peel and biochar sample. The Eager Xperience Data Handling Software was used to automatically calculate the high heating value (HHV) and lower heating value (LHV), both of which were given in kcal/kg (in this paper it was converted to MJ/kg).

2.2.2.3 Elemental analysis

The durian peel and biochar samples were prepared for XRF analysis by pressing the obtained powder. The inorganic element of three durian peel samples was analyzed using the semi quantitative analysis of elements by combusting with TGA using X-ray fluorescence spectrometer (XRF), Zetium, PANalytical. The quantitative analytical program is optimized for elements in the range of Oxygen to Uranium. The X-ray generator operates at a voltage between 20 - 60 kV and a current

of 40–100 mA.

2.2.2.4 Cellulose, hemicellulose, and lignin

According to Georing and Van Soest (1970), Van Soest (1991) and AOAC (2000), Cellulose, hemicellulose, and lignin of the durian peel was analyzed, using acid detergent fiber (ADF), neutral detergent fiber (NDF) and, acid detergent lignin (ADL) determination (Vázquez Encalada and Segura Campos, 2021). The dried durian peel was refluxed for 60 minutes in 100 mL of acid detergent solution for the ADF process (a combination of cetyltrimethylammonium bromide technical grade in 1 L 1.0 N H₂SO₄). Subsequently, the samples that had adhered to the side of the refluxed beaker were washed with an acid detergent solution. A vacuum filter was used to filter the refluxed sample through a fritted glass crucible. To achieve a complete fiber transfer into the crucible, the beaker was washed with hot distilled water. Before vacuum drying, the residues were rinsed twice with 40 ml of acetone. To determine the weight of ADF, the fiber residues were then dried overnight in a hot-air oven at 100 °C. NDF and an ADL content were calculated using the same method as ADF. A neutral detergent solution is made by mixing EDTA (disodium dihydrogen ethylene diamine tetraacetate), distilled water, sodium borate, lauryl sulfate, 2-ethoxyethanol, and disodium phosphate. The solution's pH was maintained between 6.9 and 7.1. The extractive free sample was treated with a 100 mL neutral detergent solution. The extractive free durian samples (the preparation method is described in Vázquez Encalada & Segura Campos (2021) report were obtained by extracting dried biomass in a Soxhlet apparatus. ADL was measured by adding a 72 % H₂SO₄ solution (100 mL) to the ADF sample. The sample was then burned for two hours at 500 °C in a muffle furnace. The amount of hemicellulose was estimated by subtracting NDF from ADF. The difference between ADF and ADL was used to calculate the cellulose fraction.

2.2.2.5 Thermal decomposition analysis

Thermal analysis of the durian peel samples was carried out by using Thermogravimetric analyzer, TGA8000, Perkin Elmer. Prior to the TGA experiment, 10 mg of dried durian peel powder was collected in a small platinum crucible and then thermally purged under a continuous inert nitrogen gas (N₂) atmosphere with high

purity (99.99%) under a temperature range of 50 to 1000 °C and a 5 °C/min heating rate to evaluate the thermal decomposition of the lignocellulosic material as measured by the mass loss.

2.2.2.6 FT-IR analysis

The chemical functional groups presented from the three durian peel samples were investigated by using the Fourier Transform Infrared Spectrometer (FT-IR), Vertex70, Bruker with KBr pellet techniques. The chromatogram of absorbing infrared light was obtained in the middle of the spectrum range 4,000-400 cm^{-1} .

2.2.2.7 Biochar characterization

1) pH and electrical conductivity (EC)

Before determining the pH and EC, the 1 g biochar was mixed with 20 mL deionized water and shaken for 90 minutes on the shaker (International Biochar Initiative, 2015). Then, the pH and EC of the solution were determined by pH/Conductivity meter (EZ-9909SP, Water quality meter) calibrated with standard buffer solutions (pH 4.0, 7.0 and 10.0) and standard conductivity solution (1413 $\mu\text{S}/\text{cm}$).

2) Surface area and pore diameter

Firstly, the biochar was degassed at 250 °C in a vacuum condition for 24 h. The porous structure parameters were determined from the nitrogen adsorption isotherm using an automatic Micromeritics ASAP 2460 surface area and porosity analyzer. The specific surface area was calculated using (Brunauer, Emmett and Teller) BET method. Total pore diameter was determined by estimating the amount of nitrogen adsorbed at a relative pressure of p/p° 0.99.

2.2.2.8 Pyrolysis liquid characterization

1) Physicochemical characteristics

The pH and EC were measured using a pH/Conductivity meter (EZ-9909SP, Water quality meter). The specific gravity was measured using a glass hydrometer at 20 ± 0.1 °C. The amount of water in pyrolysis liquid was determined using the Karl Fischer titration method base on ASTM E203 (Volumetric KF Titration, V30S, Mettler-Toledo, Switzerland).

2) Chemical composition

The chemical composition of the pyrolysis liquid product was identified by GC-MS (GC 7890B, MSD 5977A, Agilent Technologies, USA) with VF-WAXms column (30 m x 250 μ m internal diameter x 0.25 μ m film thickness). The samples were diluted with methanol with 1:10 ratio. The conditions for gas chromatography (GC) were as follows: carrier gas, helium at 2.00 mL/min flow rate, split injection mode at 200 °C. The oven temperature profile was established as follows: initial 60 °C hold time of 2 min, 60-250 °C at 5 °C/min, with the final hold time of 10 min resulting in a total run time of 50 min. The volume of sample injected was approximately 2 μ L. The MS analysis was obtained under 230 °C at 70 eV. The relative contents of compounds were calculated by the corresponding peak area.

2.2.3 Design of experiments

The experimental design type as a central composite design (CCD) is widely used to investigate the synergistic impact of factors on a target parameter, often in combination with response surface methodology. In this study, the experimental design with three variables and three levels was used to improve the slow pyrolysis conditions to process durian peel, using Minitab 20.4 software, based on the observed responses (biochar and pyrolysis liquid yields). The three manipulated variables were pyrolysis temperature (A), cooling temperature (B), and holding time (C), as shown in Table 2.2. Pyrolysis temperatures of 300, 450, or 600 °C were set according to the thermal property of durian peel analyzed by TGA. The cooling temperatures, the first at -5 °C was selected as the lowest cooling temperatures possible to condense the pyrolysis liquid without water frozen problem, the second (10 °C) is the representative of the temperature of the water chiller, while the third (25 °C) represents the atmospheric temperature. Regarding the holding time, Zhang et al. (2015) investigated that holding times of 1, 2 and 4 h during biochar production from straw did not significantly affect the biochar properties (Zhang et al., 2015). Therefore, the shorter and narrower holding times of 30, 60, and 90 were chosen for this study. The design contained a total of 20 experiments, with 8 cube points and 6 axial points with 6 replicates to ensure the accuracy of the experiment.

Table 2. 2 Experimental variables and their levels

Variable	Unit	Symbol code	Levels of variable		
			-1	0	1
Pyrolysis temperature	°C	A	300	450	600
Cooling temperature	°C	B	-5	10	25
Holding time	min	C	30	60	90

The data were analyzed using Minitab 20.4 software, optimizing the biochar and pyrolysis liquid yields in the slow pyrolysis. The analysis of variance (ANOVA) of response surface regression, factorial plots, contour plots, surface plots, and response optimization were applied to biochar and pyrolysis liquid yields from the test runs, assessing the quality of the model fits, while an analysis of residuals was performed to assess model adequacy.

2.2.4 Economic analysis

The economic analysis of the commercial product of biochar and pyrolysis liquid from durian peel was performed using the annual cost method for a small industrial scale of 200 kg/day durian peel feed (daily durian peel generation of the community enterprise group).

The economic analysis was computed using Microsoft Excel® (version 365) software. The analysis included calculating the net present value (*NPV*) and the internal rate of return of the project (*IRR*) as shown in Eqs. (2.2)–(2.3) (Reniers et al., 2016).

$$NPV = \sum_{t=0}^T \left(X_t / (1+r)^t \right) \quad (2.2)$$

where X_t net cash inflow-outflows during a single period in year t , T is The number of time periods, and r is the discount rate. The *IRR* is rate of return for which the *NPV* is zero. This can be expressed as follows:

$$NPV = \sum_{n=0}^T \left(X_n / (1+IRR)^n \right) = 0 \quad (2.3)$$

CHAPTER III

RESULT AND DISCUSSION

3.1 characteristics of durian peel

3.1.1 Physical and chemical characteristics

The physical and chemical characteristics of three type of durian peels are presented in Table 3.1. Moisture content (3.45-8.71 wt.%) and volatile matter (69.42-73.97 wt.%) of three durian peels showed statistically significant differences. Whereas fixed carbon and ash content of PDP and Bacho durian peels are similar, but exhibit a little bit lower compared to the fixed carbon and ash content of MDP. The moisture content relates to the moisture equilibrium during durian peel sample storage. Higher moisture contain in biomass will require more energy to remove the humidity during pyrolysis process. The fixed carbon content of the biomass can be related to the anticipated yield of solid (biochar) produced during the devolatilization process. It is the carbon found in the material that remains after volatile materials are driven off (Speight, 2015). The characteristics of durian peel varied by type, age, growth conditions and location. The volatile matter and fixed carbon found in durian peels reported by Ngabura et al. (2019) and Tan et al. (2017) were higher than those found in s this study while ash content was similar.

The higher heating value (HHV) ranged 13.81-14.45 MJ/kg and lower heating value (LHV) ranged 12.63-13.21 MJ/kg were found for the three durian peel. The higher concentrations of C and H increases in material energy density, which is directly related to biomass heating value. Normally, both molar ratio of H/C and O/C increasing heating value at molar ratio of H/C increased and O/C decreased. In this study, the three durian peel sample shows H/C and O/C ratio of 1.65-1.69 and 0.81-0.82, respectively (all samples did not differ significantly). The HHV of MDP was 14.32 MJ/kg with an H/C value of 1.69, while the HHV of PDP was 13.81 MJ/kg with a H/C value of 1.65, representing the lowest and highest values, respectively.

Lignocellulose quantitative of the durian peel is presented in Table 3.1. Table 3.1 showed that MDP had more hemicellulose (27.38 wt. %) and less lignin (11.63 wt. %) than both PDP (hemicellulose 21.63 wt. % and lignin 14.71 wt. %) and BDP (hemicellulose 20.98 wt. % and lignin 12.91 wt. %), while the cellulose

quantitative had similar content. Report of Tan et al. (2017) had shown hemicellulose, cellulose, and lignin of 13.01, 60.45, and 15.45 wt. %, respectively (Tan et al., 2017) are found to be different from our investigation. It is essential to know the lignocellulosic composition of the biomass because the decomposition temperature varied by the chemical structure and the final pyrolysis products are highly dependent on the composition of raw material.

Table 3. 1 Characteristics of dried durian peel

		This study			Tan et al. (2017)	Ngabura et al. (2019)
Country		Thailand			Malaysia	
Province	Chanthaburi	Yala	Pattani	n.d.	Selangor	
Cultivars	PDP	MDP	BDP	n.d.	D 24	
Proximate analysis (wt. %)						
Moisture content	4.20 ^b ± 0.09	3.45 ^c ±0.04	8.71 ^a ±0.17	4.96	11.97	
Volatile matter	72.81 ^b ±0.69	73.97 ^a ±0.24	69.42 ^c ±0.28	70.28	85.00	
Fixed carbon	17.13 ^b ±0.64	18.43 ^a ±0.37	16.17 ^b ±0.39	21.65	17.00	
Ash content	5.86 ^a ±0.12	4.16 ^b ±0.09	5.70 ^a ±0.01	3.11	4.64	
Ultimate analysis						
HHV (MJ kg ⁻¹)	13.81 ^b ±0.26	14.32 ^a ±0.14	14.45 ^a ±0.10	13.79	n.d.	
LHV (MJ kg ⁻¹)	12.63 ^b ±0.23	13.09 ^a ±0.13	13.21 ^a ±0.09	n.d.	n.d.	
Nitrogen (wt. %)	0.92 ^a ±0.02	0.79 ^c ±0.01	0.87 ^b ±0.01	1.31	0.90	
Carbon (wt. %)	40.11 ^c ±0.07	40.80 ^b ±0.15	41.10 ^a ±0.09	40.98	40.86	
Hydrogen (wt. %)	5.54 ^b ±0.17	5.73 ^{a,b} ±0.06	5.80 ^a ±0.05	4.44	5.98	
Sulfur (wt. %)	0.10 ^a ±0.00	0.06 ^b ±0.00	0.07 ^b ±0.00	0.34	0.07	
Oxygen (wt. %)	43.85 ^a ±0.53	44.12 ^a ±0.48	44.51 ^a ±0.21	52.93	52.19	
H/C molar ratio	1.65 ^a ±0.05	1.69 ^a ±0.01	1.69 ^a ±0.01	1.30	1.76	
O/C molar ratio	0.82 ^a ±0.01	0.81 ^a ±0.01	0.81 ^a ±0.00	0.97	0.96	
Chemical composition (wt. % on dry basis)						
Hemicellulose	21.63	27.38	20.98	13.01	n.d.	
Cellulose	51.41	49.01	52.02	60.45	n.d.	
Lignin	14.71	11.63	12.91	15.45	n.d.	

n.d.= no data

3.1.2 Element component

The quantitative analysis of inorganic components presents in all three types of durian peels are shown in Table 3.2. The most abundant element was K (34,880-50,600 mg/kg), which is an essential nutrient that influences most of the biochemical and physiological processes to affect plant development and metabolism (Wang et al., 2013). In addition to K, the macronutrients Mg (3,013-4,260 mg/kg), Ca (2,262-4,190 mg/kg), P (1,349-3,740 mg/kg), and S (1,257-2,310 mg/kg) were detected. The micronutrients of Si (912-1,640 mg/kg), Fe (230-859 mg/kg), Cl (307-420 mg/kg), Na (150 mg/kg), Mn (60-70 mg/kg), Cu (46 mg/kg), and Zn (20-31 mg/kg) were also found in the durian peel. The Fe, Mn, and Cu have an influence on new growth of durian, generating green or yellow veins and Zn has an effect on both old and new leaves, whereby a plant with a Zn shortage could have leaves on top of each other owing to decreased internodal expansion (Brian J. Alloway, 2008). The findings of this study confirmed that no heavy metals were detected in three durian peels. Therefore, biochar produce from the durian peel should contain several macro and micronutrient for growing plant. Moreover, the presence of inorganic elements in durian peel may reveal the possibility of slag, corrosion, and fouling formation during the operation at high temperature. For example at the temperatures above 700 °C, potassium was released to the gas phase as elemental potassium, potassium hydroxide, or potassium chloride, which reacted in the combustor with $\text{SiO}_2(\text{g}, \text{l}, \text{s})$, $\text{SO}_2(\text{g})/\text{SO}_3(\text{g})$, $\text{HCl}(\text{g})$, and $\text{CO}(\text{g})/\text{CO}_2(\text{g})$ (Stam and Brem, 2019).

Table 3.2 Total elemental concentration of three durian peel samples used in experiment (mg/kg)

	PDP	MDP	BDP
Potassium (K)	50,600	34,880	37,291
Magnesium (Mg)	3,840	4,260	3,013
Calcium (Ca)	4,190	4,030	2,262
Phosphorus (P)	3,740	2,990	1,349
Sulfur (S)	2,310	1,470	1,257
Silicon (Si)	1,640	1,010	912
Iron (Fe)	230	350	859
Chloride (Cl)	360	420	307
Sodium (Na)	150	n.d.	n.d.

Aluminum (Al)	80	40	38
Manganese (Mn)	70	60	n.d.
Rubidium (Rb)	50	60	199
Copper (Cu)	n.d.	n.d.	46
Zinc (Zn)	20	30	31
Strontium (Sr)	20	20	8

n.d. = not detected

3.1.3 Thermal decomposition analysis

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves obtained from TGA technique have been used to compare the pyrolysis characteristics and thermal behavior of three durian peels. In general, TGA pattern depends on the composition of biomass and pyrolysis condition. Typically, biomass is composed of cellulose, hemicellulose, and lignin. Under normal heating rates, hemicellulose pyrolysis occurs completely below 350 °C, while cellulose pyrolysis occurs between 250 °C and 500 °C, and lignin pyrolysis occurs slowly within the entire pyrolysis temperature range even over 500 °C, with no significant weight loss peak appearing (Li et al., 2004). As shown in Fig. 3.1, TG and DTG curves for three durian peel samples shows three main stages of thermal degradation. The first stage, the moisture removal or dehydration stage within the range of around 50- 180 °C are presented as 6.39, 7.82 and 8.40 % while the second peak was associated with the decomposition of hemicellulose in the ranges of 180 and 230 °C as presented by 13.90, 15.46 and 17.15 % weight loss of PDP, MDP and Bacho durian peel, respectively. The major weight loss at around 230 and 600 °C was associated with the decomposition of cellulose and some part of lignin, in which the weight loss of this major peaks was 49.37, 47.04 and 45.39% for PDP, MDP and BDP, respectively.

Pertaining to the TG and DTG curves, similar trends of the three durian peel samples by the highest peak was observed at 309, 319, and 297 °C, respectively, for PDP, MDP, and BDP (Fig. 3.1(b)). The result is similar to the findings by Aup-Ngoen and Noipitak (2020) who reported the main peak of durian peel occurs between 300 and 310 °C (Aup-Ngoen and Noipitak, 2020). In this research, MDP durian peel was chosen for further study in producing biochar and pyrolysis liquid at pyrolysis temperatures of 400 and 600 °C, which was considered from the TG peak as the

temperature achieved 80% and 90% of total weight loss, respectively.

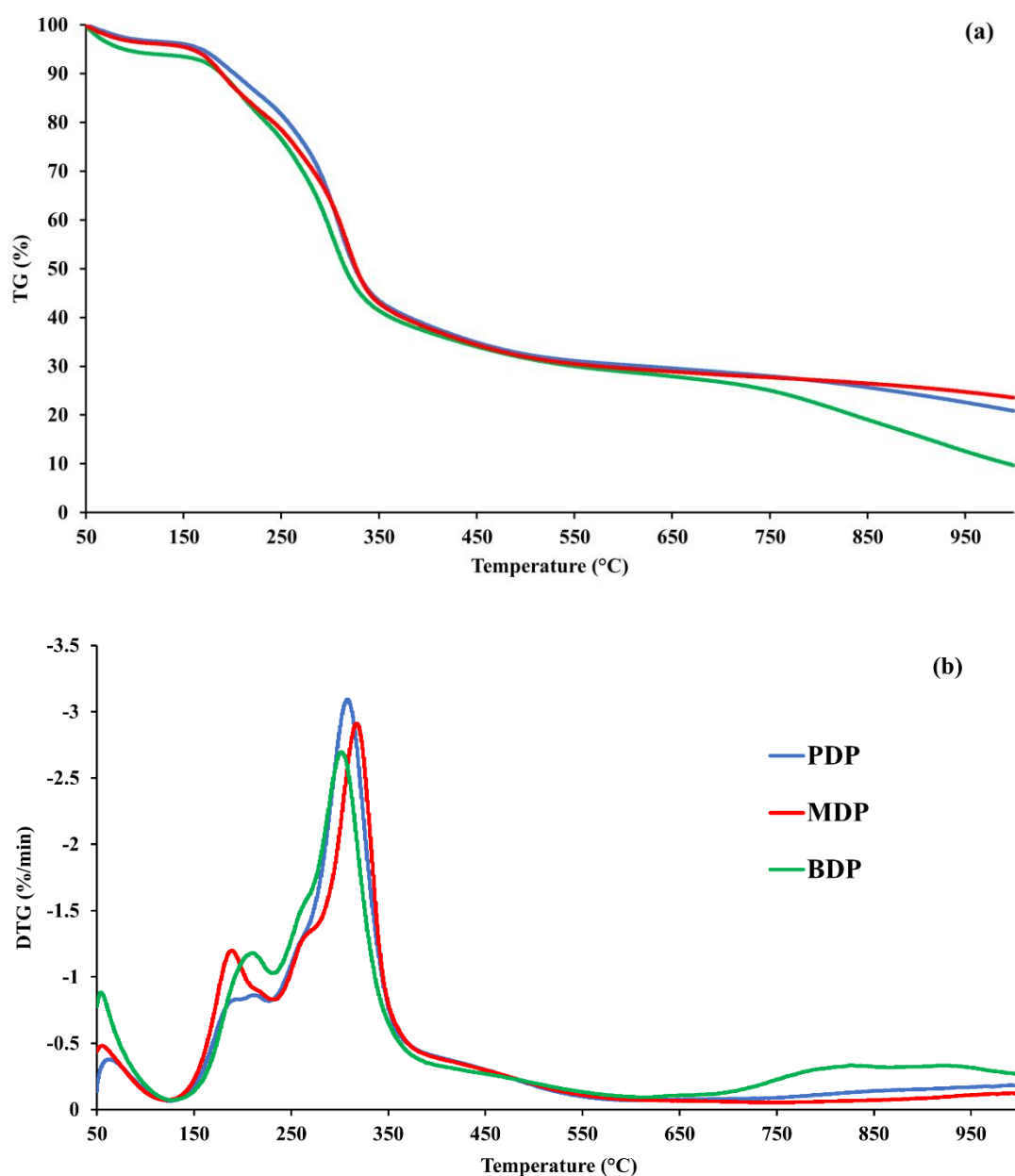


Fig. 3.1 TGA characterization of the three durian peel: (a) TG curves; (b) DTG curves

3.1.4 FT-IR analysis

Infrared spectroscopy is achieved by organic materials absorbing radiant energy in the range of $4000\text{--}667\text{ cm}^{-1}$, generating vibrational transitions in the bonds within the organic molecules. The spectrum information reveals a functionality. The FT-IR spectra of three durian peel showed similar pattern (Fig. 3.2).

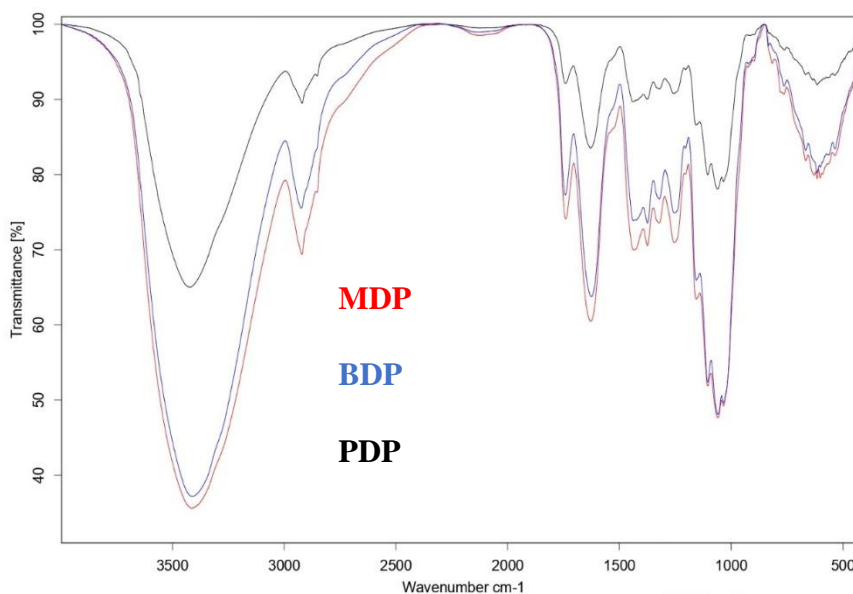


Fig. 3.2 FT-IR spectra of durian peel pattern

The spectra between 3500-3200 cm⁻¹ broad characteristics reveals O-H stretching induced by hydrogen bonding in the samples of lignin, cellulose, and hemicellulose. The C-H stretching between 2900-2860 cm⁻¹ revealed the formyl group (asymmetrical) as the weak spectra. The spectra seen around 1745 cm⁻¹ which represents C=O stretching containing saturated aliphatic, aldehyde, and ketone. The C=C stretching of aromatic is obviously seen on three samples at spectra found between 1680-1620 cm⁻¹ identifiable to carbonyl C-O stretching. Furthermore, the FT-IR spectra can be characterized as the spectrum of cellulose, hemicellulose, and lignin.

The hemicellulose, cellulose and lignin spectrum presented in 1450-1400 cm⁻¹ (Adapa et al., 2011), between 1437-1436 cm⁻¹ demonstrated -CH₂ in-plane bending vibration. Another cellulose spectrum contains three distinctive spectra: 1376-1375 cm⁻¹, indicating weak C-O stretching (Yu et al., 2007), 1322-1321 cm⁻¹, implying C-H ring in-plane bending vibrations (Schulz and Baranska, 2007; Wilson et al., 2000), and 1204-1203 cm⁻¹, which is really a cellulose spectrum (Adapa et al., 2011). The hemicellulose spectrum was two special spectra: 1257-1253 cm⁻¹, which reveals acetylated hemicellulose (Himmelsbach and Akin, 1998), and 1035-1034 cm⁻¹, which demonstrates -C-O, C=C and C-C-O vibrational stretching (Schulz and Baranska, 2007; Wilson et al., 2000). The spectrum spectra at 1105 cm⁻¹, which

indicate C-O-C asymmetric stretching and 1060 cm^{-1} , inferencing a - $\beta(1-3)$ polysaccharide of cellulose (Szeghalmi et al., 2007). Table 3.3 includes a description of all spectrum data from this and other related studies.

Table 3.3 Assignment of the FT-IR spectral characteristics of durian peel.

IR Spectra	Wavenumber (cm^{-1})				Assignment
	PDP	MDP	BDP	Aup-Ngoen and Noipitak, 2020	
1	3421	3412	3411	3338	O-H stretching
2	2919	2920	2923	2918	Aliphatic C-H stretching
3	2852	2853			C-H stretching
4	1741	1740	1742	1735	Carbonyl and carboxyl C=O stretching
5	1630	1628	1625	1601	C=C stretching of aromatic of lignin
6	1437	1436	1437	1418	-CH ₂ in-plane bending
7	1376	1375	1375		-C-O stretching
8	1321	1322	1321		C-H ring in-plane bending vibrations
9	1257	1253	1254	1246	Acetylated Hemicellulose
10	1204		1203		Weak C-O stretching
11	1158	1156	1156	1153	<i>C-O-C asymmetric stretching of cellulose</i>
					-C-O-C ring vibrational stretching
12	1105	1105	1105		-C-O stretching
13	1060	1060	1060		- $\beta(1-3)$ polysaccharide
14	1035	1034	1034	1025	-C-O, C=C and C-C-O vibrational stretching
15	761-537	816-535	923-535	896-603	Substituted aromatic group

3.2 Biochar and pyrolysis liquid yields

Table 3.4 shows the experimental conditions and the responses (biochar and pyrolysis liquid yields) from slow pyrolysis of durian peel. Different pyrolysis conditions resulted in biochar and pyrolysis liquid yields ranging from 30.06 to 56.11 % and 27.54-38.53 %, respectively. The highest biochar yield of 56.11% was obtained at 300 °C pyrolysis temperature, 25 °C cooling temperature, and 30 min. The maximum liquid amount from pyrolysis of 38.53 % was achieved at 600 °C, -5 °C, and 30 min. The experimentally determined biochar and pyrolysis liquid yield differed from the predicted average of 3.08% and 3.12%, respectively. Moreover, it was shown that the pyrolysis temperature increased, resulting in decreased in biochar yield while increased in pyrolysis liquid yield. Table 3.4 illustrates the estimated biochar and pyrolysis liquid yields from Eqs. (3.1) and (3.2), respectively.

Table 3. 4 CCD matrix, observed and predicted product yields

Run	Pyrolysis Temp. (°C)	Cooling Temp. (°C)	Holding time (min)	Biochar yield (%)		Pyrolysis liquid yield (%)	
				Observed	Predicted	Observed	Predicted
1	300	-5	30	48.68	49.29	33.00	33.04
2	600	-5	30	30.63	30.86	38.53	38.20
3	300	25	30	56.11	55.01	27.54	28.14
4	600	25	30	30.06	32.09	37.82	37.54
5	300	-5	90	48.45	46.64	32.30	33.01
6	600	-5	90	30.12	31.43	38.39	38.21
7	300	25	90	50.22	50.22	28.42	29.17
8	600	25	90	30.91	30.52	38.23	38.61
9	300	10	60	46.42	48.80	33.16	30.82
10	600	10	60	32.47	29.73	38.10	38.12
11	450	-5	60	34.33	34.22	37.28	36.68
12	450	25	60	36.88	36.62	36.15	34.43
13	450	10	30	38.59	37.16	35.59	35.26
14	450	10	90	33.99	35.05	37.76	35.78
15	450	10	60	33.17	35.01	33.62	35.53
16	450	10	60	33.86	35.01	32.92	35.53
17	450	10	60	34.86	35.01	37.89	35.53
18	450	10	60	34.05	35.01	34.40	35.53
19	450	10	60	37.03	35.01	33.68	35.53
20	450	10	60	35.90	35.01	36.64	35.53

3.2.1 Analysis of variance (ANOVA)

ANOVA can be applied to evaluate the accuracy of a model and the influence of each input variable on the response variable. Significant input variables of the model are indicated by greater F-value and sufficiently small P-value (≤ 0.05). In statistics, the F-value measures the degree of dissimilarity between samples (Fozer et al., 2019). The ANOVA results for biochar and pyrolysis liquid yield are shown in Tables 3.5 and 3.6. The biochar yield model is remarkable for having a high F-value of 32.24 and a low P-value of 0.000, whereas the pyrolysis liquid yield model has a low F-value of 4.96 and a low P-value of 0.010. Only the pyrolysis temperature is significant among all the linear input variables (pyrolysis and cooling temperatures and holding time). The pyrolysis temperature has the most influence on biochar yield with F-value 242.45 and P-value 0.000, as well as on pyrolysis liquid yield with F-value 36.82 and P-value 0.000. One square term (A^2) also affects the response, with an F-value of 13.12 and a P-value of 0.005; however, only biochar yield is affected by this term.

The values of the regression coefficient (R^2) and adjusted regression coefficient (R^2_{adj}), which theoretically can range from 0 to 100%, provide insights into the accuracy of a model. R^2 and R^2_{adj} values of more than 90% indicate that the model is accurate (Mojaver et al., 2019). High R^2 and R^2_{adj} values show a significant dependence and correlation between the observed and predicted response values. The biochar yield models' R^2 and R^2_{adj} are greater than 90 %, but for the pyrolysis liquid yield model they are lower. The predicted values were closely similar with the experimental results (Table 3.4).

The relations between the input variables and the biochar and pyrolysis liquid yield as response variables are shown below.

$$\begin{aligned} \text{Biochar} = & 109.6 - 0.2394 A + 0.340 B - 0.249 C - 0.000499 AB + 0.000179 \\ & AC - 0.00119 BC + 0.000189 A^2 + 0.00180 B^2 + 0.00121 C^2 \end{aligned} \quad (3.1)$$

$$\begin{aligned} \text{Pyrolysis liquid} = & 17.8 + 0.0618 A - 0.325 B + 0.003 C + 0.000471 AB + \\ & 0.000002 AC + 0.00059 BC - 0.000047 A^2 + 0.00013 B^2 - \end{aligned}$$

$$0.00001 C^2$$

$$(3.2)$$

Biochar and pyrolysis liquid yield can be estimated using the predictive correlations in Eq. (3.1) and Eq. (3.2) as responses, for model-based optimizing of pyrolysis parameters.

Table 3.5 ANOVA for biochar yield

Source	DF ^a	Adj SS ^b	Adj MS ^c	F-Value ^d	P-Value ^e	Remarks
Model	9	1095.90	121.77	32.24	0.000	Significant
Linear	3	940.76	313.59	83.03	0.000	Significant
A	1	915.66	915.66	242.45	0.000	Significant
B	1	14.33	14.33	3.79	0.080	Not significant
C	1	10.77	10.77	2.85	0.122	Not significant
Square	3	137.53	45.84	12.14	0.001	Significant
A ²	1	49.54	49.54	13.12	0.005	Significant
B ²	1	0.45	0.45	0.12	0.737	Not significant
C ²	1	3.26	3.26	0.86	0.374	Not significant
2-Way Interaction	3	17.61	5.87	1.55	0.261	Not significant
AB	1	10.08	10.08	2.67	0.133	Not significant
AC	1	5.22	5.22	1.38	0.267	Not significant
BC	1	2.31	2.31	0.61	0.452	Not significant
Error	10	37.77	3.78			
Lack-of-Fit	5	27.48	5.50	2.67	0.152	Significant
Pure Error	5	10.29	2.06			
Total	19	1133.66				
R ²		96.67				
R ² _{adj}		93.67				

(A=pyrolysis temperature, B=cooling temperature, and C= holding time)

^a degree of freedom

^b adjusted sum of squares

^c adjusted mean of squares

^d the ratio of two variances, or technically, two mean squares.

^e the probability that a particular statistical measure

Table 3. 6 ANOVA for pyrolysis liquid yield

Source	DF ^a	Adj SS ^b	Adj MS ^c	F-Value ^d	P-Value ^e	Remarks
Model	9	162.856	18.10	4.96	0.010	Significant
Linear	3	147.868	49.29	13.51	0.001	Significant
A	1	134.322	134.32	36.82	0.000	Significant
B	1	12.860	12.86	3.53	0.090	Not significant
C	1	0.686	0.69	0.19	0.674	Not significant
Square	3	5.452	1.82	0.50	0.692	Not significant
A ²	1	3.063	3.06	0.84	0.381	Not significant
B ²	1	0.002	0.00	0.00	0.980	Not significant
C ²	1	0.000	0.00	0.00	0.993	Not significant
2-Way	3	9.536	3.18	0.87	0.488	Not significant
Interaction						
AB	1	8.968	8.97	2.46	0.148	Not significant
AC	1	0.001	0.00	0.00	0.987	Not significant
BC	1	0.567	0.57	0.16	0.702	Not significant
Error	10	36.477	3.65			
Lack-of-Fit	5	17.222	3.44	0.89	0.547	Significant
Pure Error	5	19.254	3.85			
Total	19	199.333		0.89		
R ²	81.70					
R ² _{adj}	65.23					

(A=pyrolysis temperature, B=cooling temperature, and C= holding time)

^a degree of freedom

^b adjusted sum of squares

^c adjusted mean of squares

^d the ratio of two variances, or technically, two mean squares.

^e the probability that a particular statistical measure

3.2.2 Diagnostic plots

Diagnostic plots such as the normal probability plot, histogram, versus fits, and versus order were used to assess the validity of the model. Figs. 3.3 and 3.4 show the normal probability and the residual plots of the models for biochar and pyrolysis liquid yield, respectively. The data are normally distributed if the points on the plot are relatively close to the straight line. As demonstrated in Figs. 3.3(a) and 3.4(a), the experimental points on the normal probability plot of residual values were satisfactorily aligned, indicating a normal distribution of fitting errors. Next, histograms were applied to illustrate the findings in Fig. 3.3(b) and 3.4(b). Residue

histograms demonstrate the distribution of residuals over all observations. The figure shows a nearly symmetrical histogram (bell-shaped, i.e., normally distributed errors). Fig. 3.3(c) and 3.4(c) show the residuals with the versus fits (predicted response). The residuals are randomly distributed at about zero, indicating that the error variance is constant. In Fig. 3.3(d) and 3.4(d), the residuals are presented in the order of the relevant observations. The residuals appear to be distributed randomly around zero, and all the other points in Fig.3.3(d) and Fig. 3.4(d) are distributed between +2.5 to -

2.

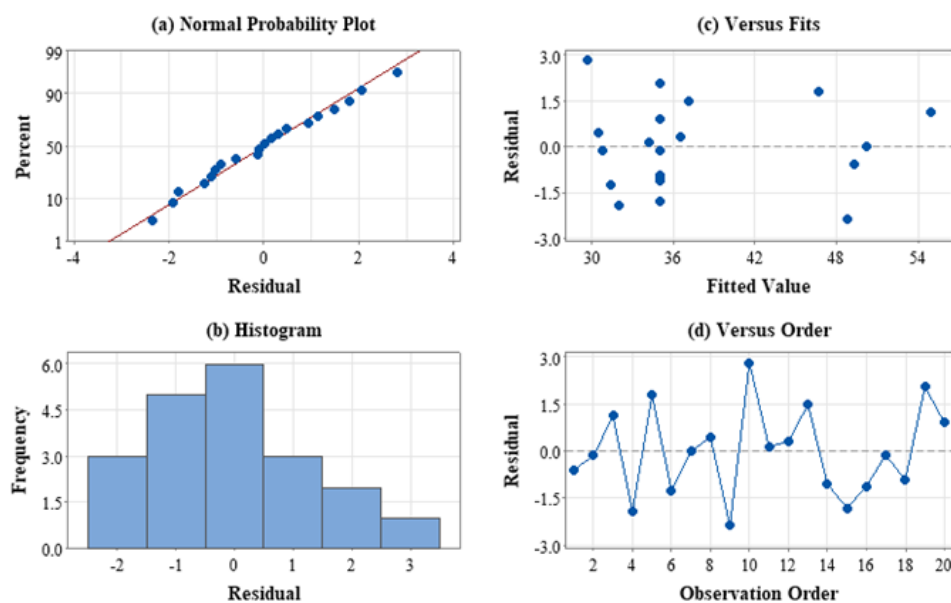


Fig. 3. 3 Residual Plots for biochar yield

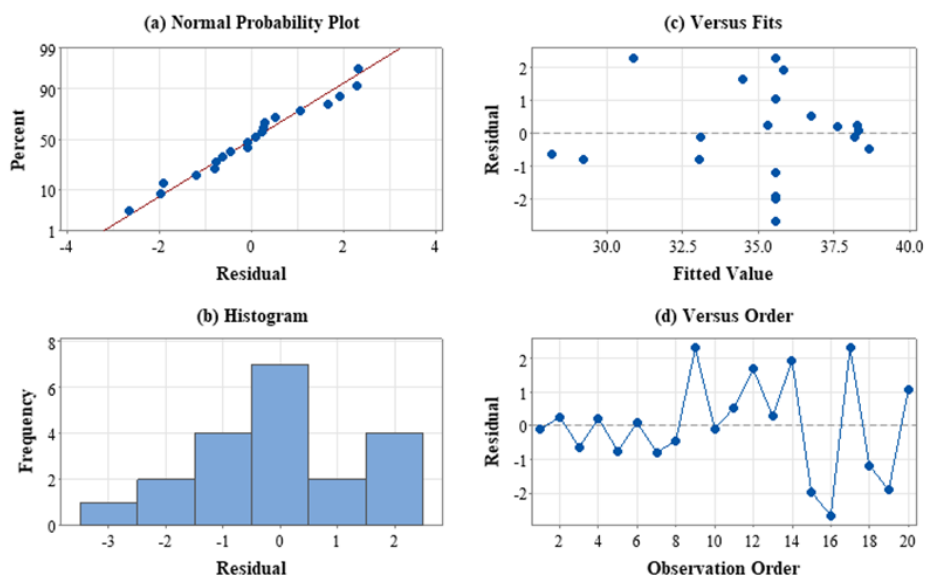


Fig. 3. 4 Residual Plots for pyrolysis liquid yield

3.2.3 Effects of input variables on the product yields

The variations of biochar and pyrolysis liquid yields with input variables, i.e., pyrolysis temperature, cooling temperature, and holding time, are shown in Fig. 3.5. The pyrolysis temperature was varied from 300 to 600 °C, and as the pyrolysis temperature increased the biochar production decreased, while the pyrolysis liquid yield increased. Increasing pyrolysis temperature improves decomposition of lignocellulosic material by fragmentation and hydrolysis, and produces volatile recombination products, resulting in a greater pyrolysis liquid yield. Furthermore, as demonstrated in Fig. 3.5, varying the cooling temperature or the holding time did not significantly impact biochar or pyrolysis liquid production (Tables 3.5 and 3.6).

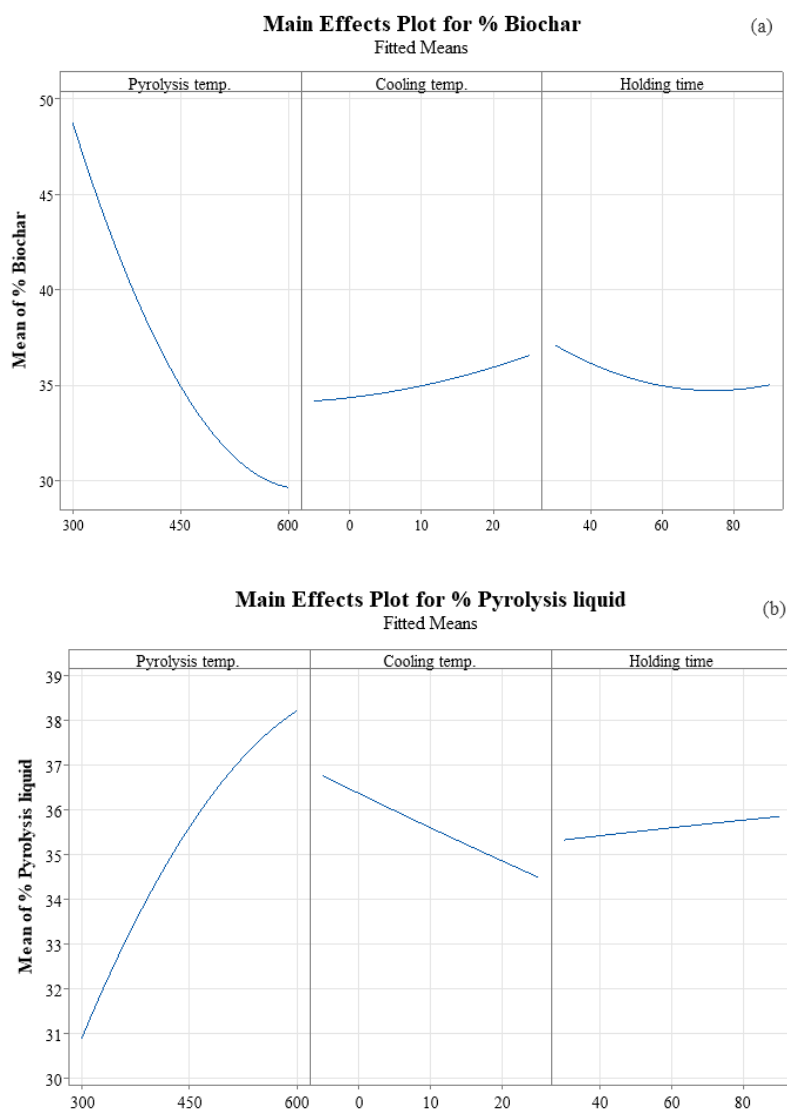


Fig. 3.5 Effects of input variables on (a) biochar yield, and (b) pyrolysis liquid yield

3.2.4 Response surface plots

In order to assess the effects of the three experimental variables on biochar and pyrolysis liquid yield, the value of one variable was kept at a fixed value, and the effects of the other two variables were analyzed, as shown in Fig. 3.6 and 3.7. Fig. 3.6(a) and 3.7(a) show the influence of pyrolysis temperature and cooling temperature on the yield of biochar and pyrolysis liquid at a holding time of 60 min. By increasing the pyrolysis temperature, the biochar yield decreased, and the pyrolysis liquid increased, primarily because higher temperature promoted the thermal decomposition of durian peel and generated gaseous products. Moreover, the yield of biochar and pyrolysis liquid was in the range of 48.68% (-5 °C) to 56.11% (25 °C)

and 33.00% (-5 °C) to 28.42% (25 °C) for pyrolysis temperature 300 °C. In contrast, the yield was between 30.63% (-5 °C) to 30.91% (25 °C) of biochar and pyrolysis liquid between 38.53% (-5 °C) to 38.23% (25 °C) for pyrolysis temperature 600 °C, respectively. These findings indicated that the cooling temperature did not influence biochar yield but pyrolysis liquid yield. The influence of holding time and pyrolysis temperature on biochar and pyrolysis liquid yield at the cooling temperature of 10 °C was shown in Fig. 3.6 (b) and 3.7(b), respectively. With an increase in holding time from 30 to 90 min for a pyrolysis temperature of 300 °C, the biochar yield decreased from 56.11% to 48.45%. Pyrolysis liquid increased from 27.54% to 32.30%, decreased from 30.63% to 30.12% of biochar yield, and increased from 37.82% to 38.39% of pyrolysis liquid yield. Thus, an increase in the holding time resulted in a not significant decrease in biochar yield or an increase in pyrolysis liquid when the pyrolysis temperature was fixed.

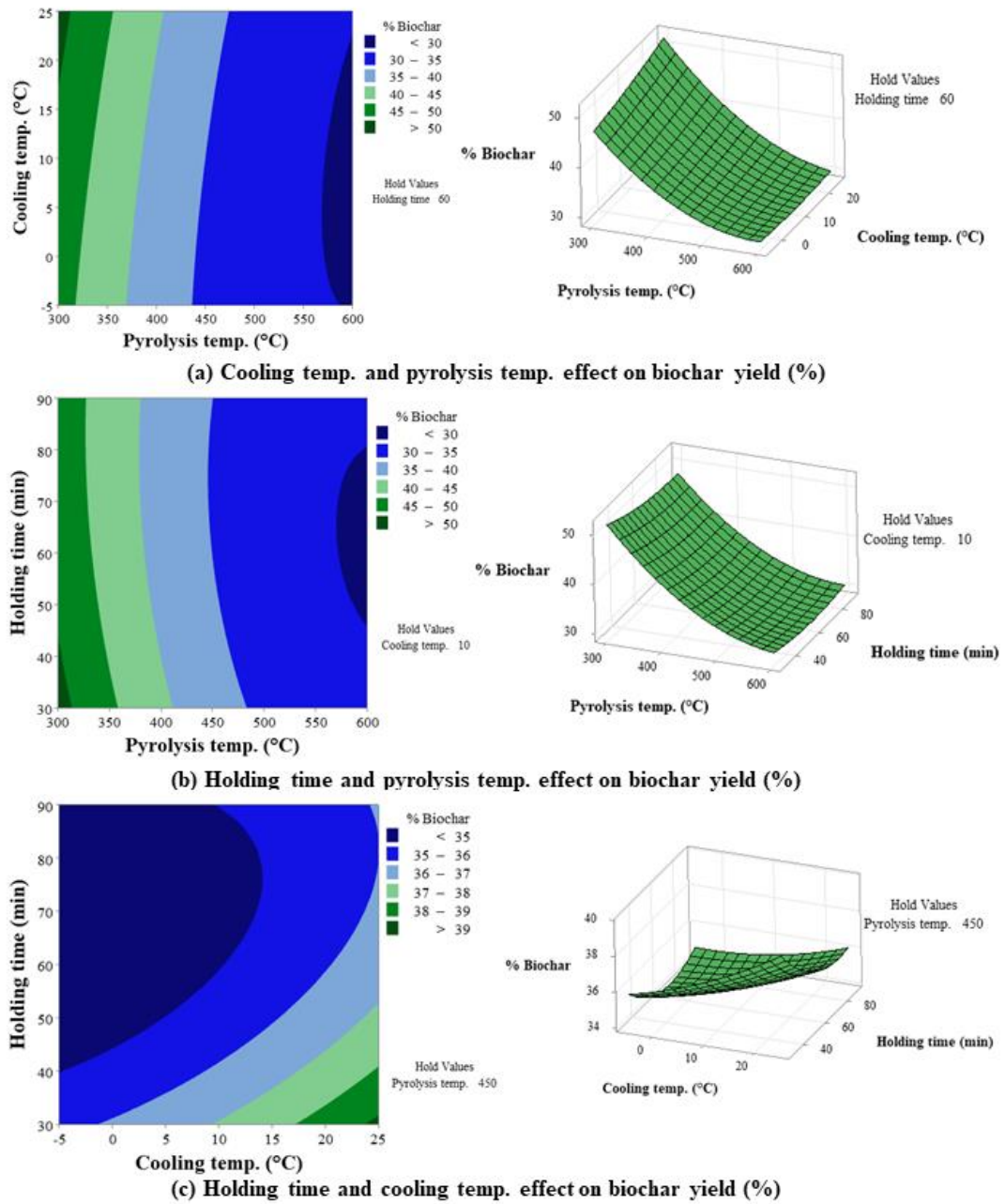
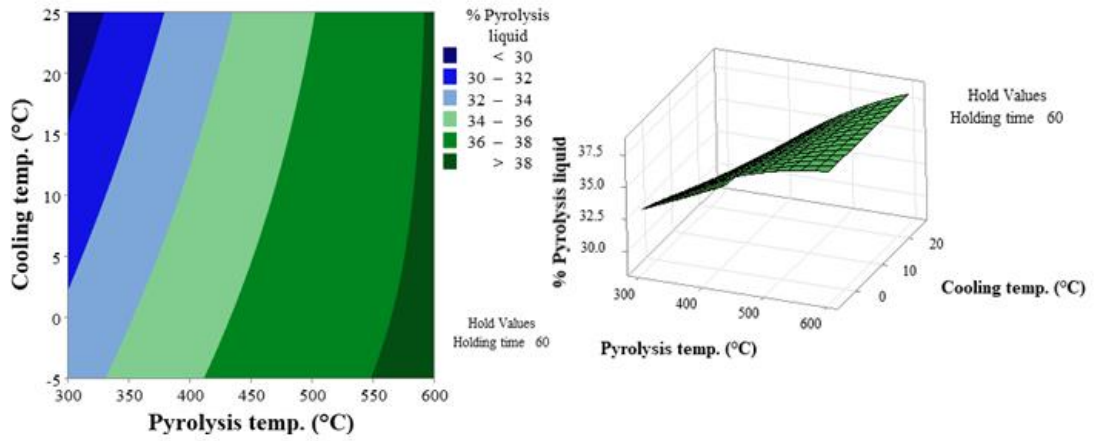
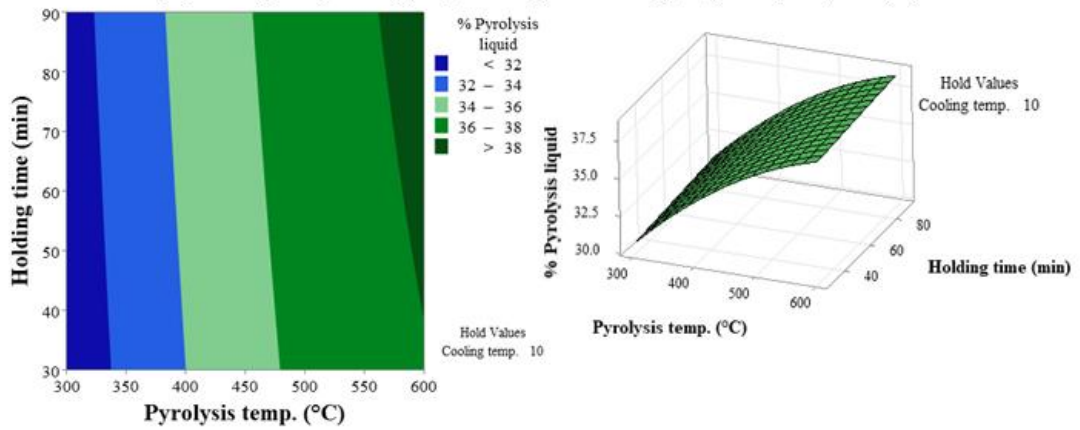


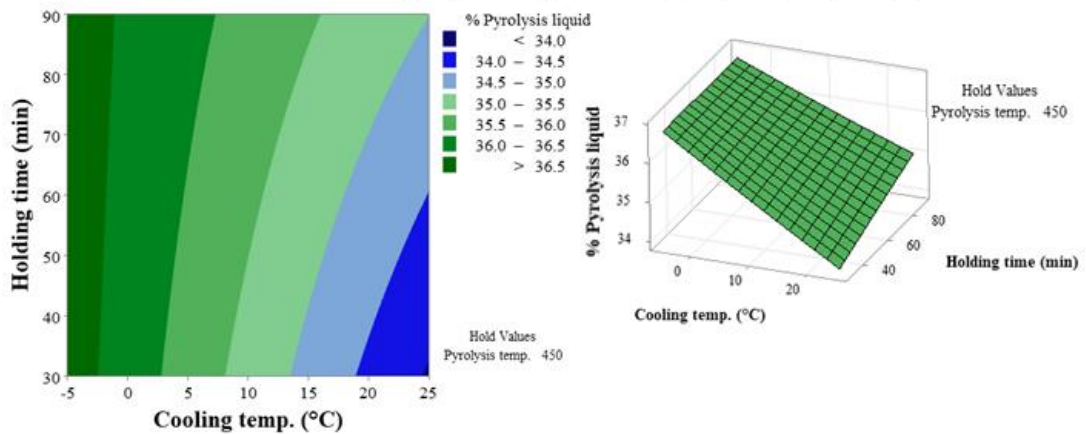
Fig. 3. 6 Contour plots and response surface plots for effects of pyrolysis temperature (°C), cooling temperature (°C), and holding time (min) on the biochar yield



(a) Cooling temp. and pyrolysis temp. effect on pyrolysis liquid yield (%)



(b) Holding time and pyrolysis temp. effect on pyrolysis liquid yield (%)



(c) Holding time and cooling temp. effect on pyrolysis liquid yield (%)

Fig. 3.7 Contour plots and response surface plots for effects of pyrolysis temperature (°C), cooling temperature (°C), and holding time (min) on the pyrolysis liquid yield

3.2.5 Model validation

The optimum condition suggested by the predicted model is 600 °C of pyrolysis temperature, 21.97 °C of cooling temperature and 83.33 min of holding time. Due to the insignificant of the cooling temperature and holding time to the pyrolysis yield, the most economical cooling temperature of 25 °C and 30 min holding time were selected for the model validation with the pyrolysis temperatures of 400 °C and 500 °C which were not the temperature points operated in the experimental design (Table 3.4). As shown in Table 3.7, the experimental biochar and pyrolysis liquid yields nearly matched the model predictions with errors of 0.25-3.47 and 0.66-0.73 %, respectively. As a result, the fitted models served as valuable tools for predicting the pyrolysis yields (biochar and pyrolysis liquid) of durian peel.

Table 3.7 Predicted and observed biochar and pyrolysis liquid yields of the model validation run.

Pyrolysis temperature (°C)	Biochar yield (%)			Pyrolysis liquid yield (%)		
	Predicted	Observed	Error	Predicted	Observed	Error
400	38.96	37.61±0.16	3.47	33.85	33.63±0.20	0.66
500	32.54	32.62±0.15	0.25	36.30	36.56±0.22	0.73

3.3 Characteristics of biochar

3.3.1 Physical and chemical characteristics

The results of proximate analysis for all samples are shown in Table 3.8. The pH and electrical conductivity (EC) measurements of biochar under different conditions gave pH in the range 9.25-11.00, and EC of 1,700, and 2,183 µS/cm. According to a report by Sun et al. (2017), when wheat straw, corn straw and peanut shell were slowly pyrolyzed, it was found that increasing the holding time at a high pyrolysis temperature had minimal influence on the biochar yield or pH (Sun et al., 2017).

Before beginning the BET analysis, it is crucial to validate that there are no traces of tar in the biochar sample by placing a spoon of biochar in a large amount of acetone in a beaker and observing whether the acetone becomes yellow or brown. No tar is present if the acetone color does not change, and the biochar is

allowed for BET analysis. Among the biochar samples, it was found some tar contained in the biochar from pyrolysis at 300 °C and 450 °C, thus their BET surface areas were not determined. The surface areas of biochars obtained at a pyrolysis temperature of 600 °C and at durations of 30 and 90 min were 1.2122 and 1.1406 m²/g, while the pore volumes were 0.0021 and 0.0019 cm³/g, respectively. The holding time substantially affects the surface area and porosity of biochar (Li et al., 2020). Similar results on the BET surface area of biochar have been reported by Zhang et al. (2018), finding that the surface area of biochar from tobacco petiole ranged within 0.45-7.51 m²/g (Zhang et al., 2018).

On a dry basis, the durian peel contained dominantly volatile matter at 76.61%, with ash content at 4.31%, and fixed carbon at 19.08%. On the other hand, the biochar produced at pyrolysis temperature of 600 °C and holding time of 90 min had the least volatile matter at 19.70 wt.%, and the highest ash content of 12.34 wt.%. Ash content illustrates the quantity of non-volatile or inorganic matter in the sample. The remaining inorganic matter in biochar presented higher ash content in biochar (6.56-12.34 wt.%) than durian peel (4.31 wt.%). The increase in ash content as a function of increasing pyrolysis temperature in the proximate analysis due to the more significant loss of volatile matter (Setter et al., 2020). At higher temperatures and longer holding times, the amount of volatile matter decreased, in contrast to the increased content of fixed carbon and ash that occurred throughout this process. Hodgson et al. (2016) reported that an increase in holding time (from 120 minutes to 360 min) decreased total carbon production and fixed carbon content (Hodgson et al., 2016). At a pyrolysis temperature of 300 °C, biochar with a lower significant proportion of fixed carbon than volatile matter was produced. The lower fixed carbon content of the sample is associated with the low carbonization degree, as biochar produced at 300 °C did not undergo complete carbonization. (Poudel et al., 2015).

The ultimate analysis results for each sample are presented in Table 3.8, and the molar ratios H/C and O/C are plotted on a Van Krevelen graph in Fig. 3.8 to illustrate the substitutability of biochar for various fossil fuels. The C concentration in biochar samples increased with increasing temperature, but the H and O contents decreased. The highest C content of 74.31 % was obtained at a pyrolysis temperature of 600 °C and a holding time of 30 min, whereas the lowest C content of 40.80 % was

found in the feedstock durian peel. The highest H and O contents were detected in the feedstock durian peel, at 5.73 % and 44.12 %, respectively, while the lowest were found in the biochar pyrolyzed at 600 °C for 90 min at 2.34 % and 13.09 %, respectively. The H and O decreases are due to deoxygenation and dehydration processes that form volatile matter, while breaking of chemical bonds is the primary cause of the separation of H and O at increasing pyrolysis temperatures (Poudel et al., 2015). The N content gradually increased with pyrolysis temperature, achieving a maximum of 1.04 % in biochar pyrolyzed at 450 °C thereafter slightly decreasing.

As pyrolysis temperature increased, the molar ratios H/C and O/C decreased significantly. For example, biochar pyrolyzed at 600 °C for 90 min provided H/C and O/C of 0.38 and 0.13, respectively, decreased from the initial feedstock (durian peel) values of 1.69 for H/C and 0.81 for O/C. Samples pyrolyzed at higher temperatures gave a slower decreasing trend. The decreases in the H/C and O/C molar ratios show that carbonization and aromaticity levels were increasing (Poudel et al., 2015). The molar ratios of H/C and O/C in the pyrolyzed samples indicate their suitability as fuels, as illustrated in the Van Krevelen diagram of Fig. 3.8.

The diagram shows that the durian peel located in the biomass region shifted to peat (biochar produced at 300 °C), lignite (biochar produced at 450 °C), and coal (biochar produced at 600 °C) regions. A preferential selection of biochar samples based on pyrolysis temperature would conclude that biochar prepared at 600 °C is the highest quality for use as a fuel. It demonstrates that greater carbonization and the H/C and O/C molar ratios indicate it is a good substitute for coal and anthracite. Table 3.8 summarizes the higher heating value (HHV) and the lower heating value (LHV) of durian peel and biochar samples. The biochar pyrolyzed at 300 °C had the lowest calculated HHV at 19.77 MJ/kg, while that pyrolyzed at 600 °C had the highest calculated HHV at 26.55-26.59 MJ/kg. Based on the data on the energy content of fuel from the Ministry of Energy (Thailand), the LHV of all biochars pyrolyzed between 300 and 600 °C exceeded that of the lignite discovered in Thailand (10.47-18.42 MJ/kg). However, biochar can also be utilized for adsorption, catalysis, soil conditioning, fuel cell supercapacitor, and hydrogen storage, in addition to serving as an alternative fuel (Cha et al., 2016).

The surface area of biochar also depends on the type and particle size of the raw material. The International Biochar Initiative (IBI) quality standards allow for an optional declaration of surface area (International Biochar Initiative, 2012). According to IBI biochar classification tool (<https://biochar-international.org/biochar-classification-tool-interface/>), biochar having H/C molar ratio less than 0.7 could be chosen to characterize as carbon storage class. Typically, the pyrolysis of an organic substance produces multiple volatile products and leaves behind a solid residue which is often highly enriched with carbon. Therefore, the biochar derived at 300 and 450 °C pyrolysis temperature which has molar ratio of H/C higher than 0.7 were not classified as IBI carbon storage. Biochar is categorized in this approach based on the amount of organic carbon (C) predicted to persist in soil for at least 100 years (BC+100). This carbon storage value is stock BC+100 (sBC+100) and used to estimate long-term soil carbon sequestration capability of biochar. The biochar samples produced at 600 °C pyrolysis temperature and 30 min holding time demonstrate carbon storage with sBC+100 = 520 g/kg (g of C per kg of soil), this being in the range of carbon storage class 4 (500g/kg ≤ sBC+100 < 600g/kg). According to various studies, using biochar as a soil amendment enhances soil physical properties, hydrological characteristics, water content and operation efficiency, soil fertility, and plant yield. (Garcia et al., 2022).

Table 3. 8 Characteristics of biochar samples and durian peel

Holding time (min)	30			90	MDP
Pyrolysis temperature (°C)	300	450	600	600	
pH	9.25 ^c ±0.15	10.42 ^b ±0.23	10.80 ^{a,b} ±0.10	11.00 ^a ±0.10	n.d.
EC (µs/cm)	1,700 ^c ±100	1,743 ^c ±55	1,950 ^b ±50	2,183 ^a ±76	n.d.
BET surface area (m ² /g)	n.d.	n.d.	1.2122	1.1406	n.d.
Pore volume (cm ³ /g)	n.d.	n.d.	0.0021	0.0019	n.d.
Proximate analysis (dry basis wt. %)					
Volatile matter	59.78 ^a ±0.41	42.13 ^b ±0.92	20.14 ^c ±0.09	19.70 ^c ±0.26	76.61±0.28
Fixed carbon	33.66 ^c ±0.39	48.84 ^b ±0.95	68.04 ^a ±0.07	67.97 ^a ±0.31	19.08±0.37
Ash	6.56 ^d ±0.02	9.03 ^c ±0.04	11.81 ^b ±0.02	12.34 ^a ±0.06	4.31±0.09
Ultimate analysis (wt. %)					
C	56.70 ^c ±0.16	64.56 ^b ±0.03	74.31 ^a ±0.23	74.40 ^a ±0.14	40.80±0.15
H	5.22 ^a ±0.02	4.40 ^b ±0.02	2.47 ^c ±0.05	2.34 ^d ±0.07	5.73±0.06
O	33.82 ^a ±0.24	23.79 ^b ±0.17	13.76 ^c ±0.11	13.09 ^d ±0.25	44.12±0.48
N	0.99 ^c ±0.00	1.04 ^a ±0.01	1.02 ^b ±0.01	0.93 ^d ±0.01	0.78±0.01
S	0.08 ^c ±0.00	0.11 ^b ±0.01	0.15 ^a ±0.00	0.15 ^a ±0.01	0.06±0.00
H/C molar ratio	1.10 ^a ±0.00	0.82 ^b ±0.00	0.40 ^c ±0.01	0.38 ^d ±0.01	1.69±0.01
O/C molar ratio	0.45 ^a ±0.00	0.28 ^b ±0.00	0.14 ^c ±0.00	0.13 ^d ±0.00	0.81±0.01

HHV (MJ/kg)	20.89 ^c ±0.08	24.24 ^b ±0.04	26.59 ^a ±0.08	26.55 ^a ±0.11	14.32±0.14
LHV (MJ/kg)	19.77 ^c ±0.07	23.33 ^b ±0.09	26.06 ^a ±0.07	26.05 ^a ±0.10	13.09±0.13

a, b, c significance difference of the various factors

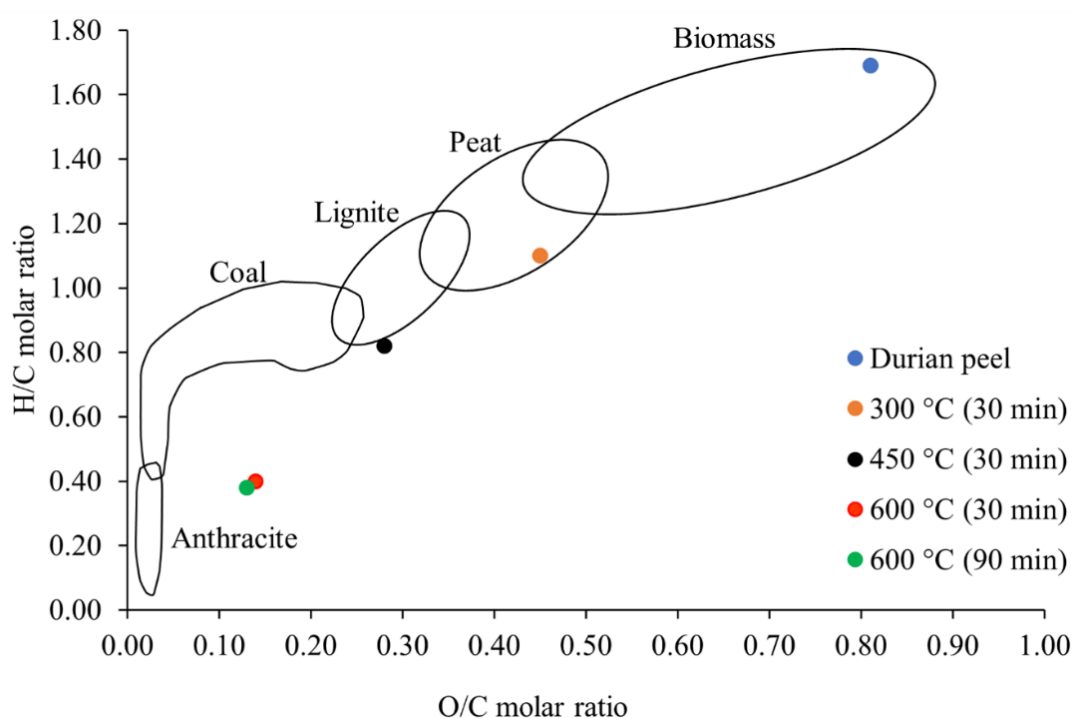
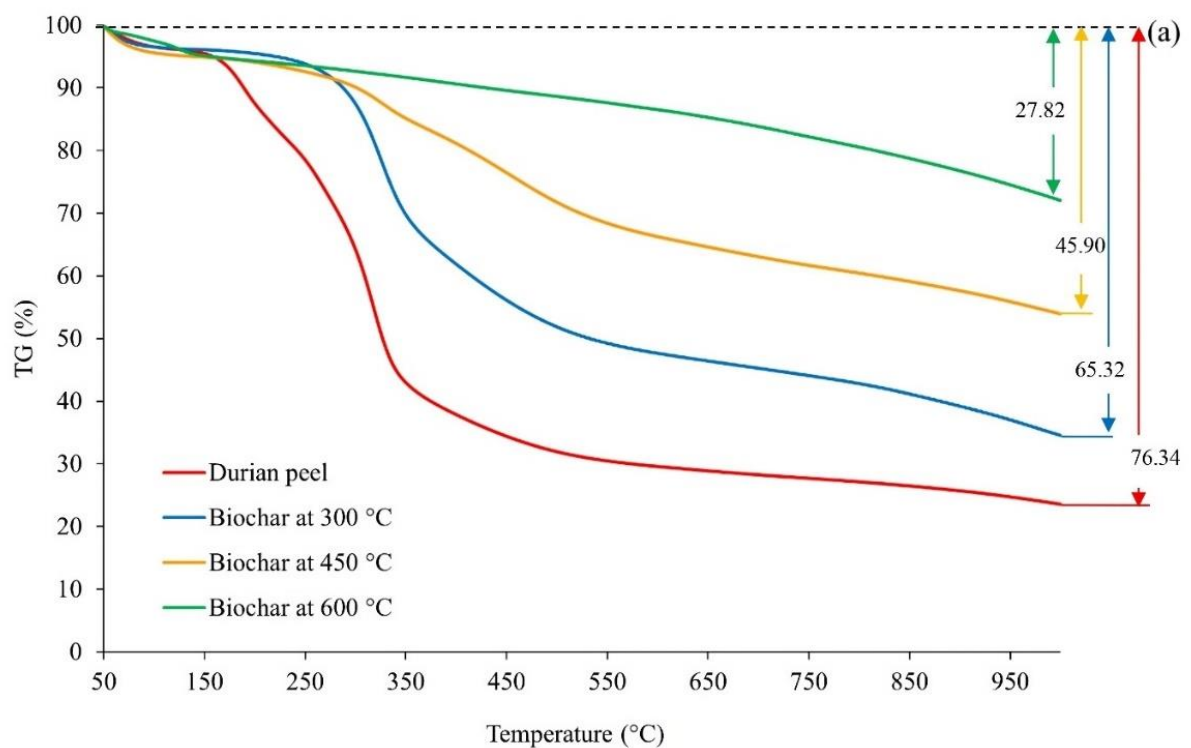


Fig. 3. 8 Van Krevelen diagram based on the molar ratios H/C and O/C

3.3.2 Thermal decomposition analysis

The thermal stability of biochar can be assessed from thermogravimetric (TG) characterization, and the results are shown in Fig. 3.9(a). The biochar had high thermal stability at the pyrolysis temperature was increased (Sun et al., 2014). The biochar samples obtained at 300, 450, and 600 °C showed total weight losses of 65.32, 45.90, and 27.82 %, respectively. The mass losses of biochar relevant to an amount of decomposed volatile matter and some amount of fixed carbon which can decomposed at the temperature up to 1000 °C during the analysis. The cellulose, hemicellulose, and lignin components of the durian peel were volatilized entirely, according to the derivative thermogravimetry (DTG) results (Fig. 3.9(b)), and the weight losses were mainly incurred by the dehydrogenation and aromatization of the biochar in addition to the decomposition of organic components (Balogun et al., 2014). The DTG curve for the durian peel had two peaks at 193 and 319 °C, while the biochar produced at the pyrolysis temperature of 300 °C revealed only one significant

weight loss peak at 328 °C. Hemicellulose pyrolysis in the raw material was responsible for the weight loss in the DTG curve at 193 °C. The thermal decomposition of the durian peel occurred over a wide temperature range (100-600 °C) by the three chemical component degradations overlap (hemicellulose, cellulose, and lignin). The DTG curve between the 110-150 °C of biochar derived at pyrolysis temperature at 600 °C is relevant to the moisture content in the biochar pore. Lei and Zhang (2013) report that biochar with enhanced micro-porosity ideally has higher water retention capability (Lei and Zhang, 2013). While, the DTG curve between the 400-550 °C of biochar derived at pyrolysis temperature at 300 and 450 °C has been identified by various authors as the decomposition of aromatic hydrocarbons of tar contained in the pore of biochar (described in BET result) (Guillh et al., 1996; Wu et al., 2010).



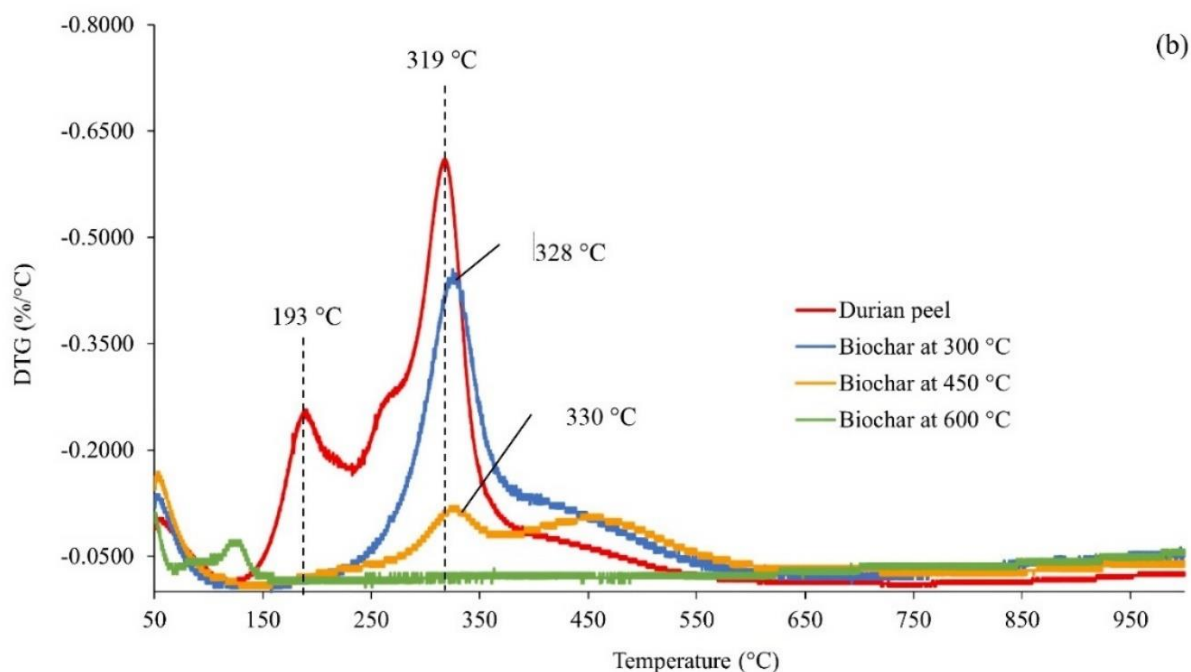


Fig. 3.9 Thermogravimetric analysis of durian peel and biochar obtained at various pyrolysis temperatures: (a) TG curves; and (b) DTG curves.

3.3 Characteristics of pyrolysis liquid

3.3.1 Properties of pyrolysis liquid

The pyrolysis liquids were obtained for the various pyrolysis temperatures and holding times. Table 3.9 displays the properties of pyrolysis liquid. Acidic pyrolysis liquid indicates the presence of acidic compounds such as acetic acid, butanoic acid, propanoic acid, etc. The pH and EC of pyrolysis liquid increased at higher pyrolysis temperatures. The pyrolysis liquid pH increased at higher pyrolysis temperatures probably due to the higher amount phenolic compounds are presented from the higher decomposition intensity of lignin component (Sangthong et al., 2022; Theapparatt et al., 2019). The specific gravity of pyrolysis liquid exhibited no significant differences, remaining constant between 1.062 and 1.065 g/mL. The water content in all pyrolysis liquids produced were not significantly different and ranged 70.72 wt.% to 72.27 wt.%.

Nowadays, many companies produce pyrolysis liquid for sale, which makes the quality of pyrolysis liquid much differently. Thus, The Thai Industrial Standards Institute (TISI) has set standards for pyrolysis liquid to control the quality

of pyrolysis liquid to be consistent and not harmful to users. The community product standards in Thailand assign a pH between 2.8-3.7 and specific gravity of more than 1.005 g/mL (Thai Industrial Standards Institute, 2010). The specific gravity value of all pyrolysis liquid conforms to Thailand's community product standards. However, the quality in terms of pH, only the pyrolysis liquid that produce at high pyrolysis temperature of 450 and 600 °C meet the standard. As mentioned earlier, pyrolysis liquid produce at lower temperature of 300 °C could have lower pH due to the higher portion of acetic acid containing in the pyrolysis liquid (Theapparatt et al., 2014).

Table 3.9 Properties of pyrolysis liquid derived at various pyrolysis temperatures and holding times

Sample		Parameter			
Holding time (min)	Pyrolysis Temp. (°C)	pH	EC (µs/cm)	Specific gravity (g/mL)	Water content (wt. %)
30	300	2.15 ^c ±0.05	1,930 ^d ±61	1.062 ^a ±0.004	69.71 ^b ±0.62
	450	2.89 ^b ±0.06	3,350 ^c ±50	1.065 ^a ±0.004	70.72 ^{a,b} ±0.67
	600	2.95 ^b ±0.05	5,300 ^a ±100	1.065 ^a ±0.002	72.27 ^a ±0.99
90	600	3.21 ^a ±0.04	3,550 ^b ±50	1.065 ^a ±0.003	70.78 ^{a,b} ±1.12
Community Product Standards of Thailand		2.8 - 3.7	-	>1.005	

3.3.2 Chemical composition

The compositions of pyrolysis liquid identified by using GC-MS. Pyrolysis liquid is a very complex mixture that contains hundreds of chemical compounds in a wide range of molecular weights. The results were accepted when the constituents with a match percentage > 85% were identified. Table 3.10 shows the total number of 81 main compounds of pyrolysis liquids (run No. 10, in Table 3.4) which can be categorized into hydrocarbon, alcohols, carboxylic acid, ester and aldehyde, ketone, amine and amide, furan and pyran, pyridine, and aromatic. While, the main component of pyrolysis liquid from Chinese fir waste as a biomass showed class of acids, phenols, ketones, aldehydes, and alcohols (Lu et al., 2019)

Many studies have reported on the characterization of pyrolysis liquids obtained from both slow and fast pyrolysis with highly varying variable results

depending on each raw material and experimental temperature (Lu et al., 2019; Tan et al., 2017; Theapparat et al., 2014). Acetic acid, Butanoic acid, 1-hydroxy-2-Propanone, 2-furan-carboxaldehyde, 2-hydroxy-methyl-2-Cyclopenten-1-one, and Phenol, 2,6-dimethoxy- were the top 6 high area percentage chemical compounds shown in both pyrolysis liquid samples. However, similar groups of compounds were reported detected in the pyrolysis liquid. The pyrolysis liquid from mangosteen, rambutan, and Langsat brushwood waste represents acetic acid with a peak area of 23.22%, 24.58%, and 23.98%, respectively. The total organic acid peak area is 29.1%, 29.65%, and 29.61%, respectively (Theapparat et al., 2019). According to Kim et al. (2008), most of the contact poison qualities of pyrolysis liquid are caused by the presence of acetic acid, which can destroy the permeability of an insect's cuticle, resulting in its death (Kim et al., 2008). Other volatile fatty acids, including formic acid, valeric acid, and propanoic acid, have also been demonstrated to be termiticides (Yatagai et al., 2002).

Some of the important components discovered in this study included hydroquinone, and catechol. Vanillin has been utilized in the production of medicines, cosmetics, and other fine chemicals as a chemical intermediary. Hydroquinone is used in a variety of industries and occupations, including dermatological (Nordlund et al., 2006). Catechol component summarily utilized as a raw material in the production of polymerization inhibitors, perfumes, medicines, insecticides, dyes, and in the dyeing and tanning of fur and leather, as well as photographic developers, deoxygenating agents, and analytical reagents (Fiege et al., 2000). According to Suresh et al. (2019), another investigation showed the presence of vanillin and catechol in pyrolysis liquid derived from softwood (Suresh et al., 2019), while Ma et al. (2014) identified hydroquinone components in pyrolysis liquid from *S. chinensis* residue as a raw material (Ma et al., 2014).

Additionally, in the literature review, the chemical of pyrolysis liquids contains various compounds, including acetic acid and short-chain acids, non-aromatic ketones, furans, sugar monomers, and oligomers (holocellulose derivatives), as well as methoxyphenols (lignin derivatives) (Urrutia et al., 2022). Yang et al. (2016) found that highly phenolic compositions in the pyrolysis liquid product from *Litchi chinensis* can be used as an antioxidant activity comparable to the reference

standards (vitamin C and butylated hydroxyl toluene) at the same dose (Yang et al., 2016). Similarly reported by Zhu et al. (2021), pyrolysis liquid promotes crop growth. It enhances biological and abiotic resistance of crop by finding the highest relative phenols, derivatives, and organic acid content (Zhu et al., 2021). Therefore, the pyrolysis liquid produced in this student could be further applied as plant stimulants. Moreover, pyrolysis liquid has numerous usages including insect repellents, plant growth promoters, plant fertilizers and feed additives, antifungal and antibacterial agents, and herbicides (César et al., 2019).

Table 3.10 Identified compounds in durian peel pyrolysis liquid at different pyrolysis temperature

No.	Component RT	Compound name	Component RT	Formula	% Area of total
Hydrocarbon					-
1	4.887	1-Butene, 3,3-dimethyl-		C ₆ H ₁₂	-
Alcohols					3.23
2	4.612	2-Propen-1-ol		C ₃ H ₆ O	0.06
3	15.053	Propylene Glycol		C ₃ H ₈ O ₂	0.12
4	16.053	1,2-Ethanediol, monoacetate		C ₄ H ₈ O ₃	0.35
5	17.922	2-Pentenal, 2-methyl-		C ₆ H ₁₀ O	0.18
6	29.515	1,2,3-Propanetriol		C ₃ H ₈ O ₃	2.52
Carboxylic acid, ester, and aldehyde					<u>36.34</u>
7	10.200	Acetic acid, hydroxy-, methyl ester		C ₃ H ₆ O ₃	0.11
8	11.434	Acetic acid		C ₂ H ₄ O ₂	26.56
9	13.200	Formic acid		CH ₂ O ₂	0.56
10	13.835	Propanoic acid		C ₃ H ₆ O ₂	2.30
11	16.922	Butanoic acid, 2-methyl-		C ₅ H ₁₀ O ₂	0.48
12	18.422	Pentanoic acid		C ₅ H ₁₀ O ₂	0.07
13	19.207	2-Butenoic acid, (E)-		C ₄ H ₆ O ₂	0.18
14	27.084	Butanoic acid, anhydride		C ₈ H ₁₄ O ₃	3.78
15	28.110	2-hydroxypropane-1,3-diyl diacetate		C ₇ H ₁₂ O ₅	0.28
16	28.958	Glycerol monoacetate, mixture of 2 isomers		C ₅ H ₁₀ O ₄	1.81
17	31.608	Benzoic acid		C ₇ H ₆ O ₂	0.16
18	33.680	Vanillin		C ₈ H ₈ O ₃	0.05
19	39.357	Syringaldehyde		C ₉ H ₁₀ O ₄	-
Ketone					<u>13.44</u>
20	5.897	Cyclopentanone		C ₅ H ₈ O	-
21	6.415	Cyclopentanone, 2-methyl-		C ₆ H ₁₀ O	0.03
22	7.945	2-Butanone, 3-hydroxy-		C ₄ H ₈ O ₂	0.47
23	8.306	2-Propanone, 1-hydroxy-		C ₃ H ₆ O ₂	5.17

No.	Component RT	Compound name	Component RT	Formula	% Area of total
24	8.992	2,4-Hexadienal		C ₆ H ₈ O	-
25	9.589	2-Cyclopenten-1-one		C ₅ H ₆ O	1.11
26	9.873	2-Cyclopenten-1-one, 2-methyl-		C ₆ H ₈ O	0.33
27	9.978	1-Hydroxy-2-butanone		C ₄ H ₈ O ₂	0.92
28	12.105	2-furan-carboxaldehyde		C ₅ H ₄ O ₂	-
29	12.541	2-Cyclopenten-1-one, 3,4-dimethyl-		C ₇ H ₁₀ O	0.17
30	12.568	4,4-Dimethyl-2-cyclopenten-1-one		C ₇ H ₁₀ O	-
31	13.440	2-Cyclopenten-1-one, 3-methyl-		C ₆ H ₈ O	0.74
32	13.751	2-Butanone, 1-(acetyloxy)-		C ₆ H ₁₀ O ₃	0.12
33	13.946	2-Cyclopenten-1-one, 2,3-dimethyl-		C ₇ H ₁₀ O	-
34	14.273	2-Cyclopenten-1-one, 2,3,4-trimethyl-		C ₈ H ₁₂ O	0.03
35	18.116	4-Hexen-3-one, 4,5-dimethyl-		C ₈ H ₁₄ O	-
36	18.200	4-Hepten-3-one, 4-methyl-		C ₈ H ₁₄ O	0.08
37	19.040	1,2-Cyclopentanedione		C ₅ H ₆ O ₂	0.28
38	19.596	2-Hydroxy-3,5-dimethylcyclopent-2-en-1-one		C ₇ H ₁₀ O ₂	0.27
39	20.312	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-		C ₆ H ₈ O ₂	2.01
40	20.547	2-Cyclopenten-1-one, 2-hydroxy-3,4-dimethyl-		C ₇ H ₁₀ O ₂	0.08
41	21.682	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-		C ₇ H ₁₀ O ₂	0.65
42	26.997	2-Hydroxy-gamma-butyrolactone		C ₄ H ₆ O ₃	0.42
43	34.862	1-(3-Hydroxy-4-methoxyphenyl) ethanone		C ₉ H ₁₀ O ₃	0.19
44	35.133	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-		C ₁₀ H ₁₂ O ₃	0.37
Amine and amide					<u>2.51</u>
45	11.050	N, N-Dimethylacetamide		C ₄ H ₉ NO	0.03
45	25.485	1,3-Propanediamine		C ₃ H ₁₀ N ₂	2.48
Furan and pyran					<u>5.97</u>
47	6.837	Furan, 2-(methoxymethyl)-		C ₆ H ₈ O ₂	-
48	7.439	3(2H)-Furanone, dihydro-2-methyl-		C ₅ H ₈ O ₂	0.06
49	13.071	Ethanone, 1-(2-furanyl)-		C ₆ H ₆ O ₂	0.55
50	13.652	4-(hydroxymethyl) dihydro-2H-pyran-3(4H)-one		C ₆ H ₁₀ O ₃	0.09
51	14.697	2-Furancarboxaldehyde, 5-methyl-		C ₆ H ₆ O ₂	0.64
52	16.418	xi-3,5-Dimethyl-2(5H)-furanone		C ₆ H ₈ O ₂	0.18
53	16.639	2-Furanmethanol		C ₅ H ₆ O ₂	1.81
54	17.057	2(5H)-Furanone, 5-methyl-		C ₅ H ₆ O ₂	0.12
55	18.703	2(5H)-Furanone		C ₄ H ₄ O ₂	0.27
56	19.823	2H-Pyran-2-one, tetrahydro-		C ₅ H ₈ O ₂	0.25
57	23.088	Maltol		C ₆ H ₆ O ₃	0.72
58	30.935	1,4:3,6-Dianhydro- α -D-glucopyranose		C ₆ H ₈ O ₄	0.84
59	32.664	5-Hydroxymethylfurfural		C ₆ H ₆ O ₃	0.44
Pyridine					<u>1.46</u>
60	6.016	Pyridine		C ₅ H ₅ N	-
61	6.648	Pyridine, 2-methyl-		C ₆ H ₇ N	0.08

No.	Component RT	Compound name	Component RT	Formula	% Area of total
62	7.231	Pyridine, 2,3-dimethyl-		C ₇ H ₉ N	0.02
63	9.370	Pyridine, 2,4-dimethyl-		C ₇ H ₉ N	0.03
64	10.348	Pyridine, 3-ethyl-		C ₇ H ₉ N	0.01
65	24.518	2-Pyrrolidinone		C ₄ H ₇ NO	0.19
66	31.327	3-Pyridinol		C ₅ H ₅ NO	1.13
Aromatic					<u>14.65</u>
67	20.952	Phenol, 2-methoxy-		C ₇ H ₈ O ₂	1.14
68	22.924	Creosol		C ₈ H ₁₀ O ₂	0.48
69	24.386	Guaiacol, 4-ethyl-		C ₉ H ₁₂ O ₂	0.33
70	28.718	Phenol, 2,6-dimethoxy-		C ₈ H ₁₀ O ₃	3.20
71	30.211	3,5-Dimethoxy-4-hydroxytoluene		C ₉ H ₁₂ O ₃	0.76
72	31.189	5-tert-Butylpyrogallol		C ₁₀ H ₁₄ O ₃	0.75
73	32.750	1,2-Benzenediol, 3-methoxy-		C ₇ H ₈ O ₃	0.38
74	33.334	Phenol, 2,6-dimethoxy-4-(2-propenyl)-		C ₁₁ H ₁₄ O ₃	0.09
75	35.822	Catechol		C ₆ H ₆ O ₂	2.60
76	36.897	1,2-Benzenediol, 4-methyl-		C ₇ H ₈ O ₂	0.84
77	39.854	Benzene propanol, 4-hydroxy-3-methoxy-		C ₁₀ H ₁₄ O ₃	-
78	40.151	1,4-Benzenediol, 2-methyl-		C ₇ H ₈ O ₂	1.28
79	41.042	2-Ethylbenzene-1,4-diol		C ₈ H ₁₀ O ₂	0.43
80	40.389	1-(4-hydroxy-3,5-dimethoxyphenyl) propan-2-one		C ₁₁ H ₁₄ O ₄	0.61
81	40.535	Hydroquinone		C ₆ H ₆ O ₂	1.76

In relation to the investigation of durian peel processing in this study, it is worth noting here that should be applied to another international waste or residue. The biomass with similar content of C, H, and O to durian peel for example wheat straw which has 43.60 wt.%, 6.20 wt.%, and 44.32 wt.%, the peach pulp which has 44.51 wt.%, 6.73 wt.%, and 45.38 wt.%, and the paper waste which has 40.78 wt.%, 5.73 wt.%, and 51.28 wt.%, respectively (Neves et al., 2011) might be beneficial to use the slow pyrolysis at similar operating conditions which could lead to similar profile of the pyrolysis products. However, these issues must be investigated further in the future.

3.4 Economic analysis

An economic analysis of commercial production of biochar and pyrolysis liquid from durian peel was performed using the annual cost method. The annual cost is the sum of the fixed costs and operating costs of the complete pyrolysis

process. The operating condition, product yields and characteristics of run No. 4 (Table 3.4, 30.06% of biochar and 37.82% of pyrolysis liquid yield) were used for the economic analysis based on the economical cooling temperature and holding time and the best product quality.

3.4.1 Fixed costs

Table 3.11 describes several assumptions that were made to estimate the annual fixed costs of the pyrolysis unit. Table 3.12 details the initial cost of the complete pyrolysis plant. The capacity of pyrolysis units (Fig. 3.10) is established for 200 kg/day durian peel having 70% initial moisture content, running 4 batches/day (2 h for each batch production). A shredder is for cutting the raw durian peel into a smaller size of 2×3 cm. The durian peel pieces are then dried in a solar dome to reduce the moisture amount to 10.0%. 50 kg of dried durian peel will be fed to the pyrolysis reactor for each cycle, and this system was continuously flushed with nitrogen at 5 L/min (total 60 min include the flushing before heating and the cool down process). LPG is used as fuel for heating to a pyrolysis temperature of 600 °C and holding for 30 min. The vapors from the decomposition of lignocellulose are carried out of the reactor by N₂ flushing to the condensation unit, and cooling water in the chiller is set at 25 °C. Moreover, additional equipment is required for operation with this unit, as shown in Table 3.12, and the sum of \$1,680.00 is designated for civil construction.

Moreover, the uncondensed product gas is suggested to be recycled to combine with LPG for heating the system for cost-saving and environmentally friendly reasons. The uncondensed product gas contains 25-39% carbon monoxide (CO), 21-29% hydrogen (H₂), 29-33% carbon dioxide (CO₂), 6-10% methane (CH₄), and 2-4% C₂-C₄ hydrocarbons (Ghenai, 2010; Waheed et al., 2013) reported that natural gas or methane fuel can be replaced with uncondensed product gas in gas turbines. Hence it is possible to safely combine uncondensed product gas with LPG using the proper designed system (Ghenai, 2010). However, the saving from recycling uncondensed product gas is not accounted for in the economic analysis because its exact heating value was not measured in the batch experiment.

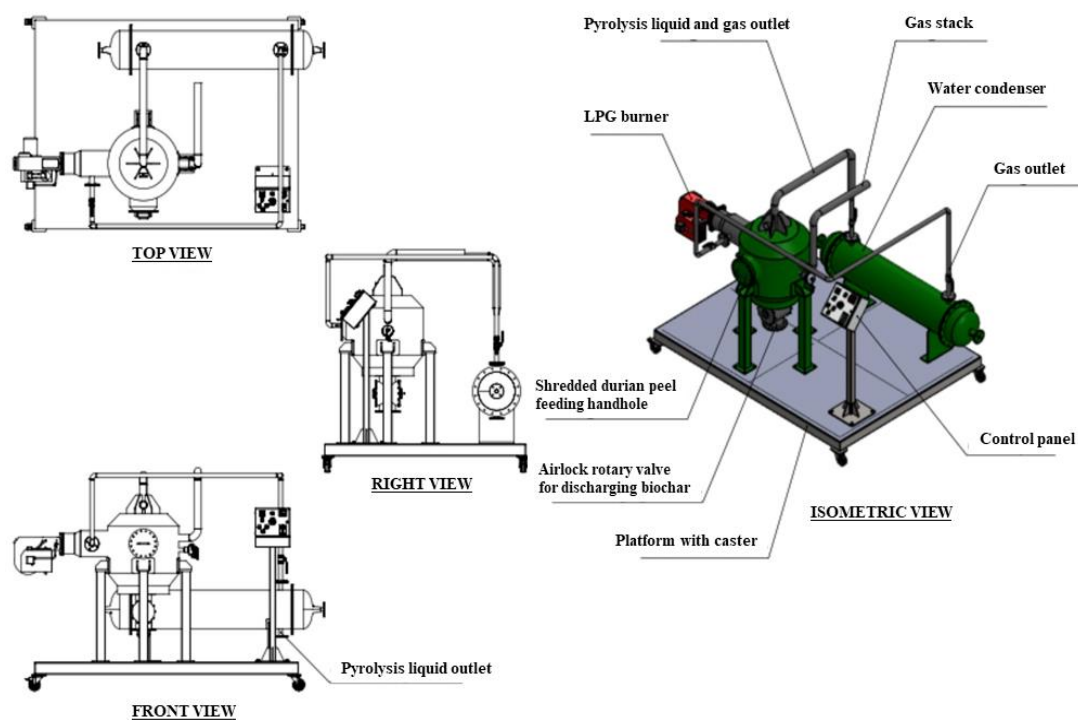


Fig. 3. 10 The batch pyrolysis unit model for 50 kg durian peel feed

Table 3. 11 Assumptions for pyrolysis unit

Parameter	Assumption	Unit
Financing	100	%
Pyrolysis unit availability	300	days/year
Pyrolysis unit depreciation period	10	year
Interest on investment	10	%
Capacity (9.42% moisture durian peel)	200	kg/day
Quantity of batch	50	kg
Annual capacity	60	ton
Fuel (LPG)	15.65 ^a	kg/day
Nitrogen flow (5 L/min)	1.2 ^b	m ³ /day
Electricity for chipping and grinding	900 ^c	kWh/year
Electricity for cooling	4,941 ^d	kWh/year
Cooling water	84 ^e	L/year
Antifreeze coolant	16.8 ^f	L/year
Total annual operating hours	1,800	hr

^a total heat required including 20% heat losses is 150.53 MJ/batch convert to kg LPG is 3.01 kg/batch

^b the N₂ gas usage is 5 L/min, process duration from start to finish is 60 min/batch

^c the power consumption of shredder is 15 kWh/ton biomass

^d the power consumption of chiller is 3.05 kWh and %compressor is 90%

^e the capacity of water tank is 12 L and make-up water use is 50% / month

^f in the process of using water: ethylene glycol at the ratio of 80:20 (Engineering ToolBox, 2003) for cooling water

Table 3. 12 The initial cost of pyrolysis units

Item description	Quantity	Price (USD)	Reference
Pyrolysis unit (50 kg/batch) ^a	1	16,800.00	Estimate by Siam technoscience co., ltd.
Shredder ^b	1	2,241.12	(Energy789, 2017)
Solar dome ^c	1	836.64	(Shopee, 2020)
Chiller ^d	1	1,149.12	(LAZADA, 2021a)
Equipment for products quality analysis			A. scientific equipment limited partnership
pH meter	1	134.40	
EC/TDS/Temperature tester	1	198.24	
Hydrometer	2	134.40	
Installation cost		1,680.00	10% of pyrolysis unit cost
Miscellaneous equipment		2,149.39	10% of all equipment except pyrolysis unit (Ringer et al., 2006)
		<u>Total cost</u>	<u>25,323.31</u>

^a the horizontal cylinder reactor, volume of pyrolysis unit reactor is 0.28 m³ (0.4 m diameter and 2.2 m height)

^b diameter of cutting disc is 420 mm, 200 rpm speed, 15 kW motor power, and 1.0 ton/hr capacity

^c dimension of solar dome is 2.00 × 0.85 × 1.30 m, width × long × height

3.4.2 Operating costs

The operating costs comprise repair and maintenance costs, labor costs, the cost of procuring and transporting durian peel, LPG, electricity for the shredder and chiller, DI water and ethylene glycol for the cooling system, and the cost of supplying nitrogen to the reactor. Table 3.13 presents the assumptions made to work out the operating costs of the pyrolysis unit. Table 3.14 shows the fixed and operating costs per annum and per kg of durian peel biomass feed to the pyrolysis unit.

Table 3. 13 Assumptions made to work out operating costs

Parameter	Assumption	Unit	Reference
Repair and maintenance cost	10	%	(Cheng et al., 2020)
Discount rate	10	%	(Cheng et al., 2020)
Labor (3 worker/9.18 USD/day)	8,266	USD/worker/annum	(Ministry of Labour, 2022)
LPG	0.76	USD/kg	(Ministry of Energy, 2022)
Electricity cost	0.17	USD/kW	(Provincial Electricity Authority, 2022)
DI water cost	0.43	USD/L	(Lab valley, 2022)
Antifreeze Coolant: mono ethylene glycol (MEG)	2.80	USD/L	(LAZADA, 2020)
Nitrogen cost	20.72	USD/m ³	Pattani Oxygen co., ltd.
Biomass analysis (1 time/month)	84.00	USD	
Proximate analysis of biomass	44.80	USD	
Analysis of gross calorific value of biomass	39.20	USD	
Biochar analysis: proximate (1 time/month)	182.00	USD/month	
Proximate analysis ASTM D7582	44.80	USD	
Quantitative analysis of % CHNS	98.00	USD	(Office Of Scientific Instrument and Testing, 2022)
Analysis of gross heating value (As dried basis)	39.20	USD	
Pyrolysis liquid analysis: water content (1 time/month)	106.40	USD/month	
Qualitative analysis of organic compounds	78.40	USD	
Analysis of general characteristics	2.80	USD	
Analysis of odor	2.80	USD	
Water content	22.40	USD	
Marketing fee and packaging	20	% /sales	(Wicks, 2022)

Table 3. 14 Cost analysis of the 200 kg per day capacity durian peel biomass pyrolysis unit

Item	USD/Annum	USD/ton of durian peel
Cost estimate		
A) fixed cost estimates		
Depreciation cost	2,532.33	42.21
Interest on investment	1,266.17	21.10
Sum of fixed costs	3,798.50	63.31
B) Operating cost estimates		
Repair and maintenance cost	2,532.33	42.21
Labor cost	8,265.60	137.76
LPG cost	3,576.78	59.61
Electricity cost for chopping and grinding	154.73	2.58
Electricity cost for cooling	849.46	14.16
DI water cost	36.46	0.61
Antifreeze Coolant	47.04	0.78
Nitrogen cost	7,459.20	124.32
Biomass analysis	1,008.00	16.80
Biochar analysis	2,184.00	36.40
Pyrolysis liquid analysis	1,276.80	21.28
Marketing fee and packaging	12,139.51	202.33
Sum of operating costs	39,529.90	658.83
Total cost	43,328.40	722.14
Income from pyrolysis products		
Biochar ^a	17,675.28	294.59
Pyrolysis liquid ^b	41,299.44	688.32
Total revenue	58,974.72	982.91
Payback period		1.58
IRR (%)		25.91

^a biochar quantity of 300.6 kg/ ton durian peel, price for sale is 0.98 USD/kg (Bambooreform, 2022)

^b pyrolysis liquid quantity of 378.2 L/ton durian peel, price for sale is 1.82 USD/L (LAZADA, 2021b)

3.4.3 Net revenue generation from pyrolysis of durian peel

Based on the above result at run No. 4 (Table 3.4), the pyrolysis products comprised 30.06% biochar and 37.82% pyrolysis liquid. This means one ton of durian peel can produce 300.6 and 378.2 kg of biochar and pyrolysis liquid on processing through the pyrolysis plant. Table 3.14 indicates that the total income from the sale of pyrolysis products obtained from one ton of durian peel is \$982.91, whereas

the cost of producing these pyrolysis products is \$722.14 (Table 3.14). This showed a net saving of \$260.77 for processing one ton of durian peel through the pyrolysis unit. According to data from the Bureau of Agricultural Economic Research, in 2021, the durian peel availability was 282,390 tons. If 50% of this is processed through pyrolysis units, the durian growers of the country can earn \$36.82 million per annum from durian peel. Moreover, the financial projections provide the foundation for the cash flow calculations used to determine the net present value (NPV) and internal rate of return (IRR). This paper uses function economic in the Excel program to calculate at a 10% discount rate in the ten years of the pyrolysis unit period. The NPV is positive at \$26,222.29, with an IRR of 25.91% and a discounted payback period of 1.58 years. The results indicate that, provided the assumptions made are approximately correct, the project would be profitable.

The performance of commercial biochar production was able to process 380 kg/h of woody biomass feedstock (dry basis) to produce 63 kg/h of biochar with a mean electricity demand of 4.5 kW (Severy et al., 2018). Another report shows the feedstock capacity of 0.5 ton/h at 550 °C could achieve 19-38 % of biochar yield and 38-62% of liquid yield in different biomass types (Garcia-Nunez et al., 2017). Hence, it reveals that the investigation of durian peel processing to biochar and pyrolysis liquid in current study has a potential to be commercialized.

CHAPTER IV

CONCLUSION

4.1 Summary

This study uses a slow pyrolysis process to produce biochar and pyrolysis liquid from durian peel. Firstly, the characterization of three durian peels (Monthong (MDP), Puangmanee (PDP), and Bacho(BDP)) was analyzed for optimal characteristics for the following process then MDP was chosen to be used in the slow pyrolysis process. Secondly, the central composite design (CCD) was used for an experimental design using MINITAB software to analyze the result. Finally, the economic assessment was assessed on a large scale using the optimum quality and quantity of pyrolysis products. The main output of this research can be summarized as follows:

- The physical and chemical characteristics of the three durian peels showed slight differences in the characteristics of three durian peels. Three durian peels showed statistically significant differences in moisture content (3.45-8.71%) and volatile matter (69.42-73.97%). The higher heating value (HHV) ranged from 13.81-14.75 MJ/kg, and the lower heating value (LHV) ranged from 12.63-13.21 MJ/kg found for the three durian peels. The three durian peel sample shows H/C and O/C ratio of 1.65-1.69 and 0.81-0.82, respectively. Lignocellulose quantitative of the durian peel showed that MDP had more hemicellulose (27.38 wt. %) and less lignin (11.63 wt. %) than both PDP (hemicellulose 21.63 wt. % and lignin 14.71 wt. %) and Bacho (hemicellulose 20.98 wt. % and lignin 12.91 wt. %), while the cellulose quantitative had similar content. The most abundant element was K (34,880-50,600 mg/kg).
- The slow pyrolysis process can produce valuable products, such as biochar and pyrolysis liquid. RSM was used to design biochar and pyrolysis liquid production, and the ANOVA analysis found that practically only the pyrolysis temperature affects both product yields.
- The yield of biochar was decreased, while pyrolysis liquid was increased at a high pyrolysis temperature: (1) the highest biochar yield (56.11 wt. %)

obtained at pyrolysis temperatures of 300 °C, (2) the highest pyrolysis liquid (38.53 wt. %) obtained at pyrolysis temperatures of 600 °C.

- The economic analysis of the pyrolysis process, for a capacity of 0.2 tons per day, found that the IRR of this project is 25.91%, with a payback period of 1.58 years. Therefore, this process would recycle durian waste and other agricultural waste by converting them to value-added products.

4.2 Suggestions

- The durian peel was used in the pyrolysis process, which should decrease the moisture content less than 15%.
- The particle of durian peel should not be smaller than 0.85 mm caused that obstructing the exit of the hot vapor (reactor used in this research).
- During the experiment, continuous flow of N₂ gas should be for increased yield of pyrolysis liquid.
- The condenser used in this process should be stainless condenser to protect the equipment cracking.
- The bottle used to store the pyrolysis liquid should be used in the glass bottle, and the lid should be completely closed.

APPENDIX

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Editor of Portion(s)	Manmeen, Ajchareeya; Kongjan, Prawit; Palamanit, Arkom; Jariyaboon, Rattana	Author of Portion(s)	Manmeen, Ajchareeya; Kongjan, Prawit; Palamanit, Arkom; Jariyaboon, Rattana
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Volume / Edition	203	Issue, if Republishing an Article From a Serial	N/A
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List of Publication and Proceeding

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