# Microwave Pyrolysis Induced Bio-Oil, and Supercritical Fluid Extraction Bio-Phenol from Pyrolyzed Bio-Oil

Kanokporn Jansuwan

**A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Energy Technology Prince of Songkla University 2022**

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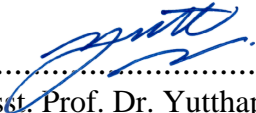**Author**           Miss Kanokporn Jansuwan
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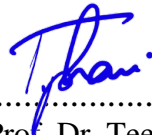
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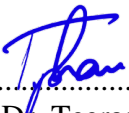

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**ชื่อวิทยานิพนธ์**    การผลิตน้ำมันชีวภาพด้วยกระบวนการไมโครเวฟไพโรไลซิสและการสกัดฟีนอล
ชีวภาพด้วยกระบวนการของไหลวิกฤตยิ่งยวดจากน้ำมันชีวภาพ

**ผู้เขียน**            นางสาวกนกพร จันทร์สุวรรณ

**สาขาวิชา**       เทคโนโลยีพลังงาน

**ปีการศึกษา**     2565

## บทคัดย่อ

งานวิจัยนี้เป็นการพัฒนาระบบไมโครเวฟไพโรไลซิส เพื่อใช้ในการศึกษาการผลิต
น้ำมันชีวภาพจากกะลาปาล์มโดยใช้ถ่านกัมมันต์เป็นวัสดุดูดซับพลังงานไมโครเวฟ ซึ่งออกแบบการ
ทดลองโดยใช้โปรแกรม Minitab ชนิด $2^k$ full factorial design: $2^3$ และได้ศึกษาหาสภาวะที่
เหมาะสมของกระบวนการฯ ซึ่งปัจจัยที่ใช้ในการศึกษา ได้แก่ อุณหภูมิ อัตราส่วนของกะลาปาล์มต่อ
ถ่านกัมมันต์ และระยะเวลาที่ใช้ในการไพโรไลซิส โดยพบว่าสภาวะที่เหมาะสมที่ทำให้ได้ปริมาณ
น้ำมันชีวภาพดิบสูงสุด คือ ที่อุณหภูมิ 700 องศาเซลเซียส ใช้อัตราส่วนกะลาปาล์มต่อถ่านกัมมันต์
เท่ากับ 80:20 และระยะเวลาที่ใช้ในการไพโรไลซิส เท่ากับ 40 นาที โดยการทำนายด้วยสมการ
ถดถอยในช่วงความเชื่อมั่นที่ 95% เท่ากับ 24.08% โดยมีค่า $R^2$ เท่ากับ 89.54% และทำการ
วิเคราะห์น้ำมันดิบชีวภาพด้วยเทคนิค (Gas Chromatograph-Mass Spectrometer; GC-MS)
พบว่าในน้ำมันชีวภาพดิบมีองค์ประกอบหลักเป็น กรดอะซิติกและฟีนอล และเมื่อนำน้ำมันชีวภาพดิบ
ที่ได้จากกระบวนการไมโครเวฟไพโรไลซิสไปสกัดด้วยกระบวนการของไหลวิกฤตยิ่งยวดด้วย
คาร์บอนไดออกไซด์ (Supercritical fluid extraction with carbon dioxide; $scCO_2$) พบว่าที่
เงื่อนไขที่อุณหภูมิ 60 องศาเซลเซียส ความดัน 350 บาร์ ระยะเวลา 30 นาที และอัตราการไหลของ
ก๊าซคาร์บอนไดออกไซด์เป็น 3.0 ลิตร/นาที ได้ปริมาณน้ำมัน $scCO_2$ สูงที่สุด เท่ากับ 56.04% เมื่อนำ
น้ำมัน $scCO_2$ ที่สกัดได้ไปวิเคราะห์ด้วยเทคนิค GC-MS พบว่าที่มีองค์ประกอบทางเคมีกลุ่มฟีนอล
และอนุพันธ์ของฟีนอลปริมาณลดลง แต่จะผลิตภัณฑ์ในกลุ่มกรดที่ไม่ได้ตรวจพบในน้ำมันชีวภาพดิบ
คือ dodecanoic, n-Hexadecanoic, และ octadecanoic และองค์ประกอบทางเคมีชนิดอื่นๆ
เพิ่มขึ้น โดยที่เงื่อนไขที่อุณหภูมิ 50 องศาเซลเซียส ความดัน 400 บาร์ ระยะเวลา 30 นาที และอัตรา
การไหลของก๊าซคาร์บอนไดออกไซด์เป็น 3.0 ลิตร/นาที สกัดฟีนอลได้ปริมาณสูงสุด เท่ากับ 36.72%
และเมื่อพิจารณาจากต้นทุนวัสดุและค่าไฟฟ้าที่ใช้ในการผลิตน้ำมันชีวภาพดิบด้วยกระบวนการ
ไมโครเวฟไพโรไลซิสพบว่ามีต้นทุนการผลิตอยู่ในช่วง 0.07-0.25 บาท/มิลลิลิตร และเมื่อพิจารณา
ต้นทุนในการสกัดหาฟีนอลชีวภาพจากน้ำมันชีวภาพดิบด้วยกระบวนการของไหลวิกฤตยิ่งยวดด้วย
คาร์บอนไดออกไซด์ที่ได้ปริมาณฟีนอลชีวภาพสูงสุดจะมีต้นทุนการผลิตอยู่ที่ 79.54 บาท/มิลลิลิตร

**Thesis Title**   Microwave pyrolysis induced bio-oil, and supercritical fluid extraction bio-phenol from pyrolyzed bio-oil

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## ABSTRACT

This research is the development of a microwave-assisted pyrolysis (MAP) system to be used in the study of the production of bio-oil from oil palm shells with activated carbon as a microwave power absorber. The experimental design was the $2^k$ full factorial design: $2^3$ to study the optimum conditions of the process. The factors were the temperature, the ratio of oil palm shells (OPS) to activated carbon (AC), and pyrolysis time. It was found that the optimum condition for obtaining the highest crude bio-oil content was at a temperature 700 °C, OPS: AC ratio of 80:20, and the pyrolysis time 40 minutes. The regression prediction in the 95% confidence interval was 24.08% with $R^2$ of 89.54%. Analyzed bio-oil by using Gas Chromatograph-Mass Spectrometer (GC-MS) found that the main components of crude bio-oil were acetic acid and phenol. Crude bio-oil obtained from microwave pyrolysis was extracted by supercritical fluid extraction with carbon dioxide ($scCO_2$) process. It found that a temperature 60°C, a pressure 350 bar, an extraction time 30 minutes, and a flow rate of carbon dioxide 3.0 liters/minute was the highest $scCO_2$ oil content 56.04%. The extracted $scCO_2$ oil was analyzed by GC-MS. The result found that phenol groups and phenol derivatives were reduced. However, the acid products that were not detected in crude bio-oil: dodecanoic, n-Hexadecanoic, octadecanoic, and other chemical constituents were found. The conditions at a temperature 50 °C, a pressure 400 bar, an extraction time 30 minutes, and a flow rate of carbon dioxide 3.0 liters/minute were the maximum extracted phenol content 36.72%. Considering, the cost of materials and electricity to produce crude bio-oil was in the range of 0.07-0.25 baht/ml, and the extraction cost with the highest bio-phenol content was 79.54 baht/ml.

# ACKNOWLEDGEMENTS

Kanokporn Jansuwan

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# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| $\varepsilon'$ | dielectric constant |
| $\varepsilon''$ | dielectric loss factor |
| AC | Activated carbon |
| BET | Surface area and porosity |
| BPA | Bisphenol A |
| FEM | Finite element method |
| FFA | free fatty acids |
| GC-MS | Gas Chromatograph-Mass Spectrometer |
| HHV | High Heating Value |
| j | Dielectric loss factor |
| LHV | Low Heating Value |
| LPM | Liters per minutes |
| Mag | Magnetron |
| MAP | Microwave-assisted pyrolysis |
| MW | MW |
| MWAb | Microwave absorbers |
| N.H.V | Net Heating Value |
| OPS | Oil palm shell |
| scCO2 | Supercritical fluid extraction |
| SFE | Supercritical fluid extraction |
| SSR | Solid State Relay |
| wt. | Weight |
| $Y_{bio-oil}$ | Bio-oil yield |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

The world's population is constantly increasing in economic, social, and industrial development to respond to the demand of the people. Therefore, the development of fuel energy is another important factor in the subsistence of human life, due to the increased demand for fuel in the industrial and transportation sectors of energy. At present, an increasing rate of energy consumption will result in future energy shortages and more expensive. Thus, it is necessary to have a sufficient reserve of energy for a reasonable price and good quality for sustainable development and has the least impact on the environment. Consequently, agricultural waste is used to produce energy (Wei, Liang, Alex, Zhang, & Ma, 2020).

Thailand is an agricultural country with products including agricultural waste with high potential that can be used as renewable energy such as sugar cane, cassava, rice straw, corncobs, rice husks, oil palm, etc. The south of Thailand is popular for oil palm plantations. In the year 2019, There was oil palm production of 14,784,987 tons/year (Office of agricultural economics). The oil palm industry will be wasted in the form of oil palm shells, empty fruit bunch, palm fiber, etc. (Parthasarathy et al., 2022). Biomass is an organic substance that can be used to produce energy indefinitely and consists of cellulose, hemicellulose lignin, and extractive (Hasanov, Raud, & Kikas, 2020). Methods for converting biomass into energy can be distinguished as: biochemical conversion, mechanical conversion, and thermochemical conversion (Garba, 2020b).Converting biomass into efficient energy source using thermal technology can be categorized as combustion, gasification, liquefaction, and pyrolysis (Luo & Zhou, 2022).

The pyrolysis process is process of thermal degradation without the oxygen.(Garba, 2020a). It is an irreversible process. Therefore, adding value to biomass by the pyrolysis process can convert agricultural waste into products such as biochar in a solid state it is useful for use as a substrate to produce activated carbon and carbon

nanofilaments in gasification processes to obtain large quantities of hydrogen gas, etc. (Tomczyk, Sokołowska, & Boguta, 2020) In a liquid state and non-condensing gases produced can be used directly as a substitute for various fuels that provides energy (Björnsson, Pettersson, Börjesson, Ottosson, & Gustavsson, 2021). The biomass pyrolysis process transformed into a product used in the future (Huang, Chiueh, & Lo, 2016). Bio-oil obtained from the pyrolysis process can be used as fuel in boilers, diesel engines for power generation, and gas turbines, etc. (Jeong, Lee, Chang, & Jeong, 2016; Lahijani et al., 2022). In addition, Bio-oil can improve quality for use as fuel and green chemical substances such as acids, phenols, alcohol, aldehydes, ketones, furans, esters, and sugars (Panwar & Paul, 2021). The main components of bio-oil are bio-phenol a high-value chemical that can be used as a substrate for use in the production of insulating material, glue, lacquer, paint, resin, inks, dyes, perfumes, soaps and can also be used as additives in benzene, antiseptic and disinfectant (P. R. Sarika, P. Nancarrow, A. Khansaheb, & T. Ibrahim, 2020). Therefore, bio-oil quality improvement for use in the production of chemicals is important (Bridgwater & Peacocke, 2000).

Bio-oil upgrade using supercritical fluid extraction is an extraction method for fuel or high value chemicals using temperature and pressure above the critical point of the substance (Omar, Yang, & Wang, 2021). It is the state in which matter cannot be classified as a liquid or a gas (Banuti, Raju, & Ihme, 2020). This method uses a short extraction time with highly effective (Feng & Meier, 2015) features of supercritical fluids are the ability to solubility and diffusion same as gas these properties vary according to the temperature and pressure in the system and the most widely used extract in supercritical fluid processes is carbon dioxide, due to the temperature of carbon dioxide used for extraction being low (31.1℃) and pressure (73.8 bar). The carbon dioxide used for extraction can be easily disposed of by leaving it at room temperature. It is high efficiency, easy to buy, cheap in price, and non-flammable, making it suitable for extraction (Zhou et al., 2022).

## 1.2 Research objectives

1) To study the optimal condition for producing the yield of crude bio-oil from the microwave pyrolysis system.

2) To study the optimal condition for producing a yield of bio-phenol from crude bio-oil by using supercritical fluid extraction with carbon dioxide ($scCO_2$).

3) To estimate the cost of producing crude bio-oil from microwave pyrolysis and bio-phenol.

## 1.3 Scope of research

1) To study the microwave pyrolysis process of oil palm shells and activated carbon to produce bio-oil for extracted bio-phenol.

2) To study the supercritical fluid extraction with the carbon dioxide process of crude bio-oil to produce bio-phenol.

## 1.4 Expected benefits.

Pyrolysis of agricultural waste (Oil palm shell; OPS) using activated carbon (AC) as microwave absorbent material in the process of microwave pyrolysis was studied. Then, crude bio-oil extraction by supercritical fluid extraction with carbon dioxide process expected benefits from the experiment are as follows:

1) Microwave-assisted pyrolysis (MAP) system can be used to produce bio-oil.

2) Bio-phenols can be extracted from bio-oil by supercritical fluid extraction with carbon dioxide process.

3) It can value adding to agricultural waste.

# CHAPTER 2

# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Phenol

Phenol (Carbolic acid, Hydroxybenzene) is an aromatic organic compound with a benzene ring derivative attached to a hydroxy group (-OH) of at least one group. The molecular formula is $C_6H_5OH$ can be produced as a chemical and a natural substance. It has a distinctive odor pure phenol is a white crystalline solid. The product is a liquid that appears as a colorless liquid, otherwise pink or red. It has acidic properties (Budavari, O'Neil, & Heckelman, 1989).
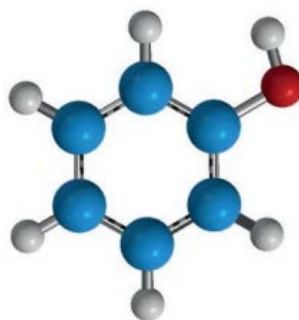


**Figure 2.1** Structure of phenols (Ouellette & Rawn, 2015)

Phenol extracted from petroleum-derived feedstocks which can be produced in large quantities (Weber, Weber, & Kleine-Boymann, 2004). It is an intermediate petrochemical produced from benzene and propylene as feedstocks. Phenol is important production of industrial commodities used in the production of Bisphenol A (BPA) and phenolic resin, the agriculture industry, the pharmaceutical industry, the dye industry, etc. (Sangthong, Phetwarotai, Bakar, Cheirsilp, & Phusunti, 2022). The process of phenol synthesis and its utilization can be shown in Figure 2.2
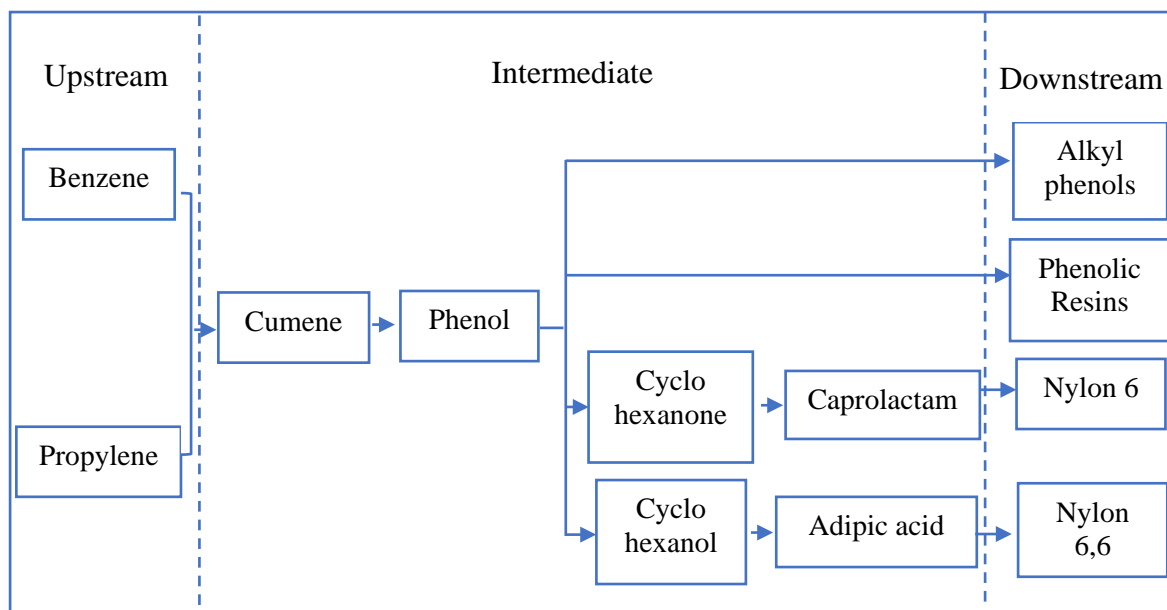
**Figure 2.2** Synthesis and utilization of phenol (Bassi & Yudken, 2009).

## 2.2 Biomass

Biomass is an organic substance obtained from plants and animals use to produce various forms of energy. Biomass can be converted into energy using thermal and chemical processes used to production energy can help reduce the cost of importing fuel from abroad. It also increases income for farmers by selling biomass to users. In addition, biomass has a lower environmental impact than fossil fuels. Generating heat or electricity using biomass as fuel to reduce the effects of greenhouse gas and acid rain caused by petroleum-based energy sources. The guidelines for the utilization of biomass can be shown in Figure 2.3

**Thermal chemical conversion**          **Biological conversion**
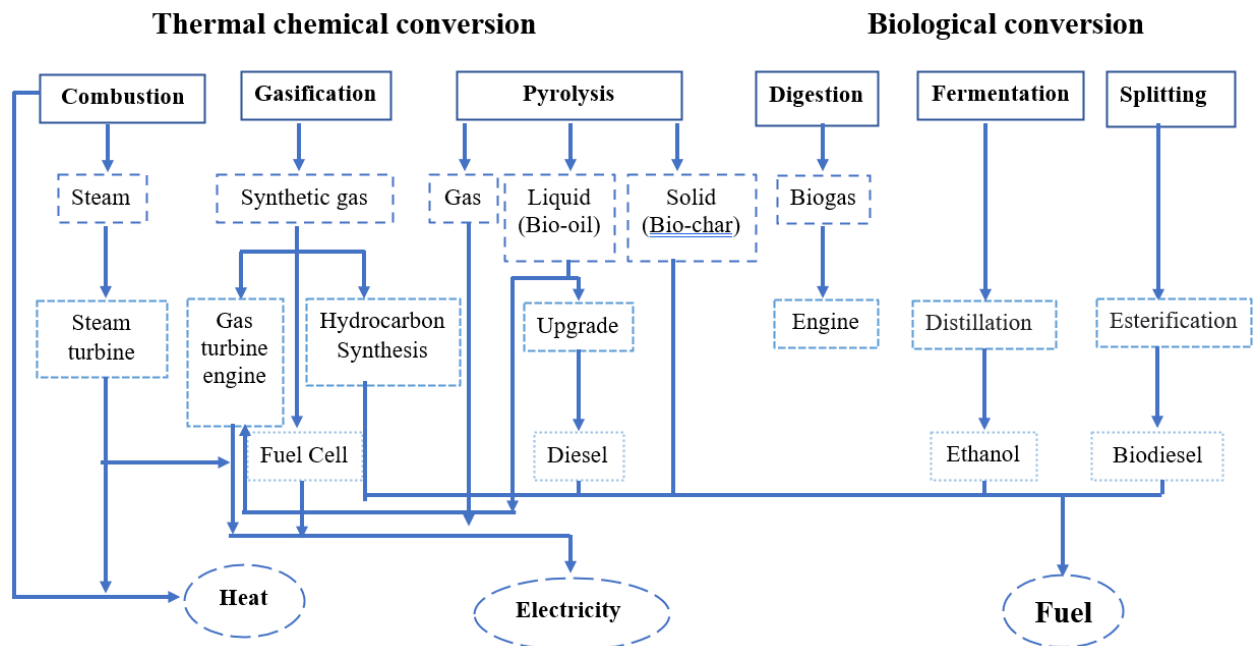


**Figure 2.3** Guidelines for the utilization of biomass (Neto et al., 2019).

### 2.2.1 Structure and composition of biomass

The structure and composition of biomass are cellulose, hemicellulose, lignin, organic matter, and other inorganic minerals. Each type of biomass has a different composition depending on the type and growth of the plant, which is shown in the following details.

### 2.2.1.1 Cellulose

Cellulose has the molecular formula $C_6H_{10}O_5$ that exists in the cell wall of plants. It was a type of polysaccharide carbohydrate consisting of linear glucan chains that are linked together by β-1,4-glycosidic which are held together by intramolecular hydrogen bonds as intermolecular van der Waals forces. Cellulose is insoluble in water or organic solvents or weak alkaline solutions but is soluble in strong acids and alkalis. The crystal structure of cellulose is highly resistant to enzymes and acids most cellulose is a crystal or a tightly arranged structure. It can be classified according to its solubility in 3 types of high sodium solutions, namely alpha-cellulose,

beta-cellulose, and gamma-cellulose. The structural of cellulose are shown in Figure 2.4
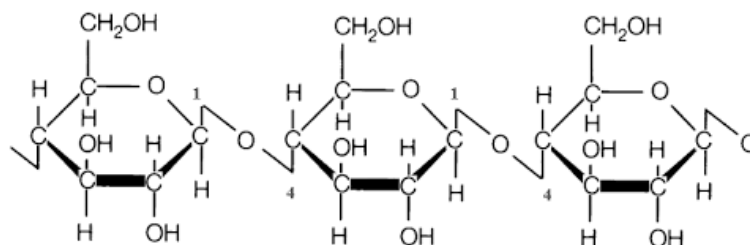


**Figure 2.4** Structure of cellulose (Acharya & Chaudhary, 2012).

### 2.2.1.2 Hemicellulose

Hemicellulose is a polysaccharide composed of sugar with 5 or 6 carbon atoms. Hemicellulose mainly consists of 2-4 sugars. The type of sugar and quantity found will depend on the type and source of the plant. Its amorphous structure has lower strength than cellulose but when bonded with cellulose, the structure is stronger. Hemicellulose is easily digested by acids or dilute bases. Hemicellulose consists of short chains of 500-3000 sugar units. In most cases, hemicellulose was found in the cell wall at about 20-30 %. The structural features of hemicellulose are shown in Figure 2.5
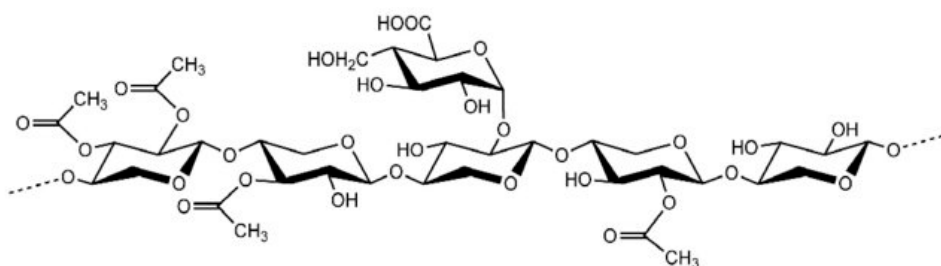


**Figure 2.5** Structure of hemicellulose (hu, Fang, Du, Luo, & Guo, 2020).

### 2.2.1.3 Lignin

Lignin has the molecular formula $C_{10}H_{12}O_4$. Lignin is a compound of carbon, hydrogen, and oxygen combined into several subunits which were aromatic substances. Lignin has properties that are insoluble in water, and not flexible but have high strength, and durability. It also has a lattice structure that serves as a link between hemicellulose and cellulose molecules together within the cell wall. This makes the plant structure highly durable. Lignin is a compound in approximately 20-30% of plant cells. The structural features of lignin are shown in Figure 2.6
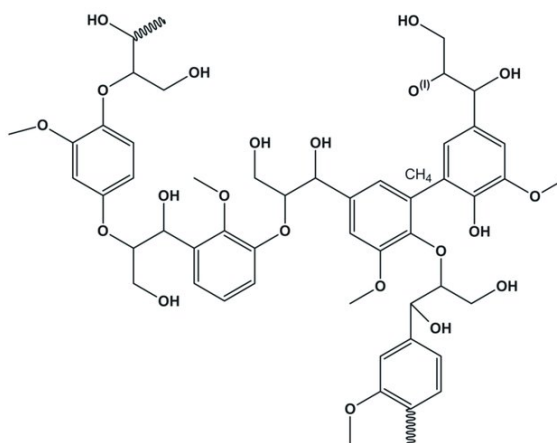


**Figure 2.6** Structure of lignin
(P. Sarika, P. Nancarrow, A. Khansaheb, & T. Ibrahim, 2020)

### 2.2.2 Biomass conversion technology

Biomass conversion enhances thermal properties and increases biomass efficiency to make it more convenient to manage and store biomass by converting biomass into liquid and gas energy using technology to improve the quality and add value. Technology is popular with the principle of thermochemical conversion and biochemical conversion.

### 2.2.2.1 Physical conversion technology

Physical conversion technology of biomass such as identification segmentation and extraction are biomass conversion processes to increase the combustion efficiency of biomass. The resulting biomass has a higher calorific

value than the normal type of biomass, reducing the costs of finding fuels for combustion that have a calorific value equivalent to biomass that was changed with this technology. This technology includes sorting, drying, size reduction, and densification technology.

### 2.2.2.2 Thermochemical conversion technology

Thermochemical conversion technology is the process of converting the chemical into thermal energy to produce forms of liquid and gas, that are easier and more convenient to use. The thermochemical can also be further classified as combustion, pyrolysis, gasification, and liquidity.

### 2.2.2.3 Biological conversion technology

Biochemistry processes are divided into 2 ways: anaerobic digestion and fermentation. Anaerobic digestion was considered a liquid waste treatment method that protects the environment and has the by-product of biogas. The fermentation process causes complex organic molecules such as starch and sugar to break down by microorganisms such as yeast and yeast into alcohol. This technology includes anaerobic digestion technology, fermentation, and distillation technology.

### 2.2.2.4 Chemical conversion technology

Chemical conversion technology uses chemical processes as the basis for the reaction to obtain chemicals so that they can be used instead of diesel. This technology includes the transesterification process.

## 2.3 Oil palm shell (OPS)

Oil palm shell (OPS) is a component of the palm fruit. It is located between the outermost husk palm fibers and the innermost palm pulp a common characteristic of OPS is brown hardwood. In the industrial production of palm oil, OPS is the residue after the extraction of palm oil from palm fruit. This qualifies as biomass fuel. OPS has a high calorific value. It is therefore popular to be used as a renewable fuel.

Most palm oil extraction processes have two methods of extraction: dry extraction and wet extraction method. Palm oil extraction includes the 4 steps as follows:

1) Sterilization using a temperature of 130 to 135 °C at a pressure of 2.5 to 3 bar period lasting 50 to 75 minutes. It will help stop the free fatty acids causing the palm to and help the palm fruit easily come off the palm bunch.

2) Stripping is the transfer of the palm bunch into a machine to separate the fruit from the bunch to make the shell separate from the seed.

3) Oil Extraction is bringing the shell to the oven at a temperature of 90 to 100 °C for a period of 20 to 30 minutes. It is passed into a twin-screw extractor machine. The liquid is passed through the twin-screw extruder. The product consists of crude palm oil 66%, water 24%, and solid 10%.

4) Clarification is the introduction of crude palm oil from extraction sent to the filter tank to separate the water and solids. Then put into the centrifuge for cleaning again and hydration of dry palm leaves to make sent to oil storage tanks for further refining or distribution.

Crude palm oil will be split into two parts, the upper part is an orange-red liquid (crude palm oil olein) of about 30% to 50% the lower part is a yellow-orange wax (crude palm oil stearin), and the amount is about 50% to 70% for the oil palm residue. Separated the fibers from the kernels and the acquired seeds are dried and cleaned then put in the crackers to separate the shells and the kernels were dried to a moisture content of more than 7 %. The oil palm residue from the palm oil extraction process can be shown in Figure 2.7

**Figure 2.7** The oil palm residue from the palm oil extraction process (Hamada, 2018).

## 2.4 Pyrolysis

Pyrolysis is the process of heating biomass by combustion in the absence of oxygen. The process of changing the chemical composition cannot be reversed during the pyrolysis process. Thus, biomass fuels decay and are transformed into 3 types of products: solids, liquids, and non-condensing gases.

The proportion and quality of products obtained from the pyrolysis process are uncertain depending on factors such as the size of biomass, composition of raw materials, starting temperature etc. Pyrolysis can be classified into 3 types: slow pyrolysis, fast pyrolysis, and flash pyrolysis.

### 2.4.1 Type of pyrolysis

#### 2.4.1.1 Slow pyrolysis

Slow pyrolysis is a process using a temperature range of 400 - 600 °C with a heating rate. The purpose of this process is to the greatest quantity of char, liquid, and gas in small quantities.

#### 2.4.1.2 Fast pyrolysis

Fast pyrolysis is a process using a temperature range of 600-650 °C with a heating rate of 10-100 °C/sec. The content products of fast pyrolysis are liquid 50-60%, solid 25-30%, and gas 15-20% depending on the material. Rapid gas condensation affects the fluid content causing biomass that undergoes rapid pyrolysis

to break down into volatile matter and condenses back into liquid products quickly, resulting in mainly liquid products. The biomass material used in this process can be any biomass material including wood chips and agricultural waste but must be dried to a moisture content of less than 10% by weight and after grinding the biomass to a smaller size to speed up the heat transfer rate in the reactor to speed up the heat transfer rate in the reactor. The maximum bio-oil product by the heating process must be achieved within a short time that the speed of condensation affects the volume of the liquid product to prevent the decomposition of bio-oil that occurs it must be cooled down immediately.

### 2.4.1.3 Flash pyrolysis

Flash pyrolysis is the process with temperature an extremely high rate of heating up to 1000 °C, and a heating rate of more than 100 °C/sec (Basu, 2010). That was like fast pyrolysis but the heat transfer and time that the material was in the reactor were shorter.

### 2.4.2 Products from pyrolysis

The products of pyrolysis are divided into 3 types of liquid products (bio-oil), solid products (bio-char), and gas products.

1) Liquid product (bio-oil) is a product that can be utilized as thermal energy, electricity, fuel in boilers, or as a precursor to the production of other chemicals. Bio-oil depends on the type of biomass and the heating method. Bio-oil can be black, brown, or reddish brown. It will consist of two-phase water-soluble components phases and bio-oil phases. The bio-oil component has different hydrocarbons depending on the type of biomass used as a substrate. The benefits of bio-oils were varied such as chemical production, heat generation, power generation, and fuel production. It was necessary to improve the quality according to the standard requirements of the oil obtained from the pyrolysis process. The reason for the need for quality improvement was that biofuel contains various kinds of chemicals and a large amount of oxygen, which in turn affects the use of biofuels in vehicles. The calculation of the bio-oil yield was determined using equations.

$$Y_{bio\text{-}oil} (\%) = [Bio{-}oil \ (g) \ / \ Biomass \ (g)] \times 100$$

Properties of bio-oil

(1) Density was an important factor in fuel selection, with increasing carbon content.

(2) Viscosity refers to the ability of an oil to resist the flow, and high viscosity means that the oil was very sticky.

(3) The cetane number (CN) was very important because it represents the amount of time the fuel burns when injected into the combustion chamber. It represents an indication of the quality of the oil.

(4) The heating value represents the heat generated by the combustion of fuel, expressed in units of heat per unit weight.

(5) The acidity was a measure of the amount of free fatty acids present in a fuel sample. Usually, the bio-oil obtained from palm had higher acidity than diesel because it had a higher amount of FFA. Biodiesel that had been blended had a lower acidity with increasing diesel fuel (Mat Yasin et al., 2017).

2) Solid product (bio-char) is a product that is mainly composition of carbon stabilizers and volatile matter of 20-30%, ash 0.5-5 %, and heating of value about 28 to 33 MJ/kg. It could be used as energy without going through any process. Solid products are contaminated with a small amount of nitrogen or sulfur. Therefore, when the char is burned, it will have a small impact on the environment. Biochar has environmental applications in sulfur dioxide ($SO_2$) pollution treatment and can be used to improve efficiency for other applications such as sorbents, activated carbon, filters, and insulation.

**Table 2.1** Standardization for bio-oils is obtained by fast pyrolysis (Anja Oasmaa, 2017).

| Property | Grade G | Grade D |
|---|---|---|
| Minimum of gross heat of combustion (MJ/kg) | 15 | 15 |
| Maximum water content (mass %) | 30 | 30 |
| Maximum pyrolysis solids content (mass %) | 2.5 | 0.25 |
| Maximum kinematic viscosity at 40 °C (mm$^2$/s) | 125 | 125 |
| Density at 20 °C (kg/dm$^3$) | 1.1-1.3 | 1.1-1.3 |
| Maximum sulfur content (mass %) | 0.05 | 0.05 |
| Maximum ash content (mass %) | 0.25 | 0.15 |
| pH Report Minimum of flash point (°C) | 45 | 45 |
| Maximum pour point (°C) | -9 | -9 |

**Note:** In the case of using fuel-grade G for industrial furnaces. In the case of using fuel-grade D for industrial or commercial kilns that require solid and low ash fuels.

3) Pyrolysis gas product is a gas with a non-condensing gas composition of gases such as carbon dioxide, carbon monoxide, hydrogen, and methane. It could also be used to generate electricity and the primary petrochemical industry because pyrolysis gas had a relatively low heating value.

### 2.4.3 Pyrolysis kinetics

Pyrolysis kinetics was the study of the speed of reactions evaluation of thermodynamic biomass conversion in pyrolysis processes (Gogoi et al., 2018). The reaction of pyrolysis kinetics was as in the equation:

$$\text{Biomass} \xrightarrow{k(T)} \text{Char+Gas+Tar}$$
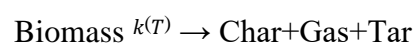
The reaction changes or pyrolysis kinetics require activation energy ($Ea$), which was the minimum energy used for chemical or physical changes to

stimulate atoms or molecules. The fast reaction because of the low activation energy. On the other hand, high activation energy results in a slow reaction.

### 2.4.3.1 The kinetics of the pyrolysis process

The kinetics of pyrolysis process consists of three mechanisms such as heat transfer, mass transfer, and chemical kinetics. This kinetic mechanism can be categorized by heat it was divided into four steps, as shown in the following:

    1) Drying stage

The drying stage is increasing the temperature of the raw material (around 100 ℃), causing some of the water in the cells to be evaporated until the heat was transferred to the raw material. The water content of raw material affects the solidification of products. The high content of water dissolves the lignin and when it cools to a solid.

    2) Initial stage

Biomass undergoes exothermic dehydration at temperatures around 100- 300 ℃, resulting in reduced molecular weights of water and gas from raw materials.

    3) Intermediate stage

The macromolecules of the material were broken down, creating vapors or producing bio-oil precursors, taking place at temperatures around 200-600 ℃. During this time most liquid products were formed.

    4) Final stage

In this stage, the second decomposition of vapors forms non-condensing charcoal and gases, taking place in the temperature range of 300-900 ℃.

The difference in pyrolysis will result in the quantity and different characteristics. In the case of OPS, when the lignin content is higher, the thermal decomposition is slower (Mushtaq, Abdullah, Mat, & Ani, 2015).

## 2.5 Microwave

A microwave (MW) is a high-frequency electromagnetic wave with a frequency range from 0.3 to 300 GHz and the corresponding wavelength from 1 to 0.001 m as shown in Figure 2.8. Electromagnetic waves propagate in space at the speed of light ($\sim 3 \times 10^9$ m/s). In general, the frequency of MW, which is used in industrial applications 915 MHz and 2,450 MHz.
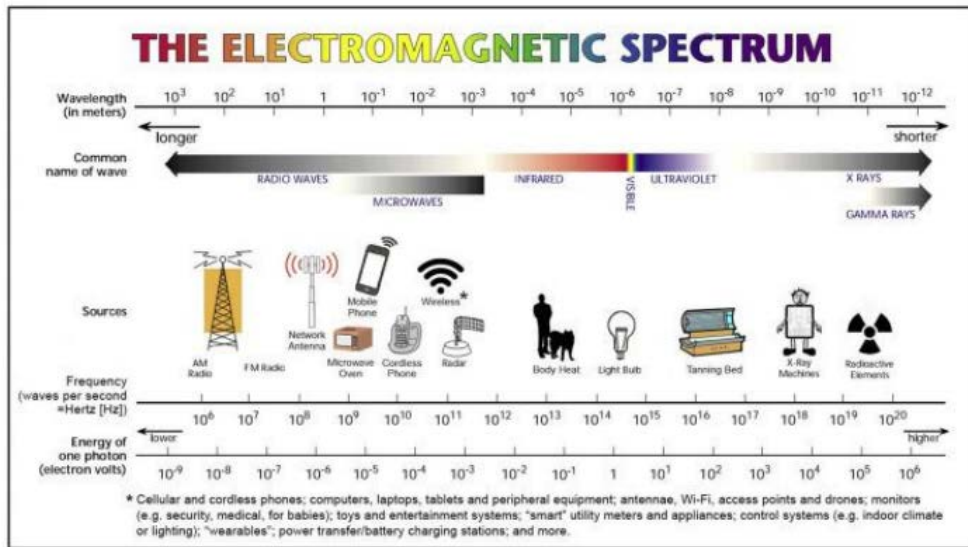
**Figure 2.8** The frequency spectrum of electromagnetic waves (Clegg et al., 2020).

Electromagnetic waves travel in space without obstructions approximating the behavior of planar waves. Electromagnetic waves are electric field components (E) and magnetic field elements (H) that oscillate in-phase and perpendicular directions. Electromagnetic waves consist of 2 components: an electric field and magnetic field that vibrate in phase and planes perpendicular to the direction of wave propagation.
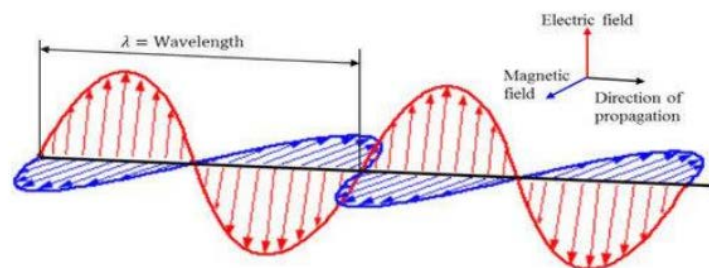


**Figure 2.9** Electric(E) and magnetic (H) field components in a microwave

(Tang, 2015).

### 2.5.1 Microwave interaction properties

Microwave interaction properties can be divided into 3 properties.

#### 2.5.1.1 Reflection

The reflection is caused by microwave energy that affects the material as a metal or metal element waves cannot pass through the metal and will reflect all back.

#### 2.5.1.2 Transmission

Transmission is caused by the fact that the microwave can penetrate non-metallic materials, including glass, plastic, paper, ceramics, wood, etc. The waves can pass through, so these materials are commonly used as a container for laying or wrapping food in a microwave oven.

#### 2.5.1.3 Absorption

Absorption is material response to microwaves by absorb microwaves and converting into heat. It is caused by the fact that the microwave affects materials containing water or moisture. The waves will be absorbed causing water molecules to absorb wave energy and convert it to heat energy including the movement of water molecules. Therefore, this capability can be determined through electro-field response analysis and magnetic response analysis. This causes heat as well. The microwave waves after being absorbed will decay immediately, there is no residue in the material.

### 2.5.2 Heat transfer of microwave heating

Heat transfer is the transfer via direct thermal energy between two objects. The heat transfer depends on the temperature of the individual entity and the medium that transmits heat energy. The basic principle of microwave heating is that the molecular structure of materials can absorb different microwaves. The molecules of the material vibrate, absorbing microwaves, and friction until heating inside the material.

When the electric charge in the material is polarized by the electric field (El Khaled et al., 2018).

### 2.5.3 Microwave absorber

Materials that absorb microwaves are called adsorbents or dielectrics can be classified into three categories based on exposure loss: high absorbent material (> 0.5), medium (0.1-0.5), and low (<0.1) the use of a microwave absorbent facilitates heat transfer to the target in the short run because microwave energy can penetrate the absorbent efficiently the particle size of the microwave absorbent affects the temperature using microwave absorbers will save energy, save the time of the process, and increase the production rate. addition, the microwave absorber also catalyzes certain chemical reactions by heating the substrate to obtain better products Lam et al. (2017). Various carbon materials such as charcoal, carbon black, and activated carbon. Activated carbon is a carbon-based material that has a very high surface area (around 1,000 $m^2$ /g) Normally, activated carbon is applied to such tasks as an odor absorber, color absorber, and filter.

### 2.5.4 Dielectric properties of microwave dielectric heating

Dielectric materials are highly polar and can store electrical charges. therefore, it is not a good conductor of electricity or electrical subjected to a material that can be dissipated as heat energy dielectric properties play a critical role in deciding the interaction between the electric field and the relative complex permittivity consists of two parts, real and imaginary, which are dielectric constant ($\varepsilon'$) and dielectric loss factor ($\varepsilon''$), respectively.

The relative complex permittivity, $\varepsilon*$ is given by.

$$\varepsilon* = \varepsilon' - j\varepsilon''$$

where $\varepsilon'$ is the dielectric constant and $\varepsilon''$ is the dielectric loss factor $\varepsilon'$ describes the material's ability to store electric energy (for $\varepsilon'$ vacuum = 1), while $\varepsilon''$ represent the material's ability to dissipate electric energy and high-frequency heating

(radio frequency), the dielectric loss factor is the primary factor in determining ability to dissipate electric energy into heat. Dehydrating materials dissipate the absorbed electrical energy into heat faster than rapidly depleting materials (Tang & Resurreccion, 2009).

### 2.5.5 The advantages of microwave heating

The microwave generates volumetric heating, but conventional heating generates from the exterior of the material. General heat generation characteristics occur when the heat is transferred from the surface of the material outside. Sometimes it can be observed that the surface of the material burns and may not distribute heat throughout the material. The heat from the microwave was generated in the total volume of the surface by the core of the material and distributed to the surface of the material (Popescu, Misawa, Ohtsu, Fujita, & Sanematsu, 2008). The heat produced by microwave was more efficient and economical than conventional heating because it can be heated directly without heating from the surrounding (Salema & Ani, 2011), (Abubakar et al., 2013). Also, microwave provides volumetric heating that was consistent and fast (Lee, Lee, Gan, Thangalazhy-Gopakumar, & Ng, 2017; Salema & Ani, 2011; Undri et al., 2015). Microwaves are widely used in various fields more efficiently compared to conventional heating. Due to its advantages in many areas such as non-contact heat, good heat transfer, high rate of heating, the heat generated within the material, easy to control (quick start and stop), and is automated, thus having a higher level of security (Y.-F. Huang, Chiueh, & Lo, 2016). Also, the formation of pollutants in secondary reaction products was reduced when microwave pyrolysis was used and the raw material moisture was greatly reduced, resulting in increased surface area. It also improves the structure of porous, because during the pyrolysis process the volatile matter was released rapidly. Table 2.2 shows the comparison between microwaves and conventional heating.

**Table 2.2** The difference between microwave and conventional heating (Yin, 2012).

| Energy conversion | Energy transfer |
|---|---|
| Volumetric heating: all materials were heated simultaneously at the molecular level. | Superficial heating: all materials were heated via convection or conduction. |
| Rapid and efficient heat generation | Slow heat generation, is inefficient, depending on the thermal conductivity properties of the material. |
| Selective: heat occurs quickly for dielectric materials. | Non-selective |
| Hotspot: The effect of the electromagnetic field or dielectric properties causes the temperature inside the material to be higher than the measured temperature in the bulk | No hot spot |
| Precise and controlled heating: power ON or OFF, power input will start and stop immediately respectively | Less controllable |

## 2.6 Bio-oil

Bio-oil from pyrolysis is a liquid that is black, brown, or reddish-brown depending on the type of biomass and the method of heating. It may have other names such as pyrolysis oil, crude oil, biofuel oil, liquid smoke, pyrolysis tar, and pyroligneous acid. Bio-oil is produced by the thermal breakdown and polymer disintegration of cellulose, hemicellulose, and lignin at high temperature then substances formed during the reaction will be carried out to inhibit the reaction by rapid cooling to avoid reactions such as decomposition or condensation with other molecules creating a new product.

Bio-oil contains compounds that are sensitive to reactions. It has different properties depending on the conditions of the pyrolysis process. Generally, bio-oil contains ingredients that can dissolve containing about 75-80 percent of organic matter by mass and another 20-25 percent of the water, bio-oil with oxygen percentage of 46-48 by mass as shown in Table 5. It can be used in the production of heat,

electricity, automotive fuels, and chemicals to use bio-oil for heating and electricity using boilers or diesel engines.

## 2.7 Supercritical fluid extraction

Supercritical fluid extraction is a state in which a substance cannot be distinguished from gaseous or liquid state. Supercritical fluid extraction to separate undesirable materials from desired products. Supercritical fluids are increasingly being used for the extraction of natural products, such as the extraction of odors, colors, and active ingredients from natural products. Carbon dioxide ($CO_2$) is the most used supercritical fluid, sometimes co-solvents such as ethanol or methanol for extraction.

**Figure 2.10** The supercritical fluid (Ahangari et al., 2021)
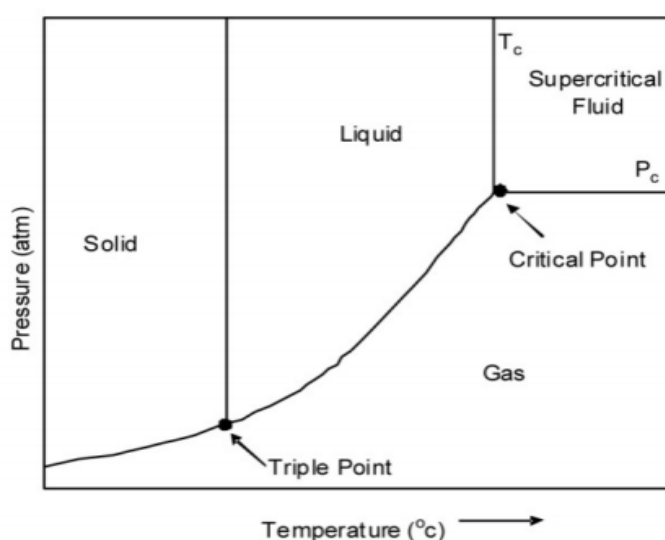


The properties of supercritical fluids that result in better extraction are shown below.

1) Transportation supercritical fluid has a low viscosity and high diffusion coefficient. It can spread evenly making the solvent dissolved into the fluid supercritical extraction area spread out to other areas easily and a high rate of mass transfer viscosity and coefficient of preparation of supercritical fluids depend on many factors such as

temperature and pressure, so temperature and pressure conditions must be adjusted accordingly for the best extraction of the required substances.

2) Solvent power property the ability of the supercritical fluid solvent is temperature dependent. The density can be reduced or increased by adjusting the temperature and pressure to the optimum state able to adjust the properties of supercritical fluids to better suit extraction.

3) Selectivity property the ability to selectively extract is another feature by adjusting the temperature and pressure to provide the optimum solubility in the desired extraction the substance is not contaminated as little as possible.

Also, the advantage of extraction using supercritical fluids is that extraction product 15 is high purity and saves the solvent used in the extraction. Suitable for the extraction of substances or products that are easily decomposed when heated.

**Table 2.3** The critical constant of some solvents used as the solvent (King & France, 1992)

| Compound | Critical temperature | | Critical pressure | | Critical density (g/mL) |
|---|---|---|---|---|---|
| | K | ºC | MPa | Bar | |
| Ethylene | 283.0 | 9.9 | 5.12 | 51.2 | 0.23 |
| Carbon dioxide | 304.1 | 31.0 | 7.39 | 73.9 | 0.47 |
| Nitrous oxide | 309.6 | 36.5 | 7.26 | 72.6 | 0.46 |
| Propane | 369.8 | 96.7 | 4.26 | 42.6 | 0.22 |
| Sulfur hexafluoride | 318.8 | 45.7 | 3.76 | 37.6 | 0.75 |
| Methanol | 513.4 | 240.3 | 7.99 | 79.9 | 0.27 |
| Water | 637.0 | 363.9 | 22.10 | 221.0 | 0.32 |
| Ammonia | 405.4 | 132.3 | 11.30 | 113.0 | 0.24 |
| n-Pentane | 469.8 | 196.7 | 3.37 | 33.7 | 0.23 |

## 2.8 Analysis cost

The cost data was very important as the first element in business administration for planning, control, and decision-making. The costs help to accurately analyze various alternatives, such as decisions about production or sales. The order acceptance sets the selling price, whether to produce it yourself or buy it. The high and fierce competition in the wine market today causes all organizations to carry out various

activities. The strategies that the competitors will use more and more every day will be cheaper sales prices and at the same time, customers need cheap products. In designing a new pyrolysis system, it must be developed to reduce the cost of pyrolysis oil production, (Y.-F. Huang, Chiueh, & Lo, 2016)

### 2.8.1 Production cost

Production cost means the total cost of production in one product period. Production costs were the sum of all three components: direct raw materials, direct labor, and production overheads. The sum of direct labor and production overhead was known as a conversion cost. Production cost analysis was very necessary for collecting, distributing, analyzing, and reporting expenses incurred in terms of production costs for the benefit of management and policy implementation of the management an economic evaluation of the required parameters for energy efficiency and assessing the impact of equipment investment (Ao et al., 2018).

# CHAPTER 3

# METHODOLOGY

## 3.1 Materials used in the experiment.

In this research, the residues from the oil palm industry, oil palm shell (OPS), were obtained from the area of Surat Thani Province the Southern Palm (1978) Co., Ltd., and Commercial grade granular activated carbon (AC) from coconut shells

## 3.2 Equipment used in the experiment.

In the experiment, the following equipment was used:

1) Microwave pyrolysis system with dimension 0.22×0.22×0.312 m. It consists of 4 magnetrons power 4,000 Watt (1,000×4 = 4,000 Watts)

2) Supercritical fluid extraction with a carbon dioxide system

3) Erlenmeyer flash quartz reactor volume 1,000 ml It has a diameter of 5.0 cm., the bottom of the flask has a diameter of 16.0 cm. and a height of 26.5 cm.

4) Biomass crusher

5) Sieve No.10 (2.00 mm), No.16 (1.18 mm), and No.20 (850 µm)

6) Hot air oven

7) Digital balance with two decimal places

8) High-temperature thermocouple type-K

9) Temperature controller SHIMAX

10) RS485

11) Solid-state relay

12) Rotameter

13) Watt-hour meter

14) Nitrogen gas ($N_2$) as commercial grade

15) Condenser system

16) Water pump

17) Hydroscopic sample dispersing agent

18) Carbon dioxide gas ($CO_2$)

19) Software Shimax

20) Glassware

21) Teflon rods

22) Metal tape

23) Rotameter

**3.3 Scope of research**

**Part 1: Microwave pyrolysis of oil palm shell and activated carbon process.**

The objectives of this research are to study the ratio of oil palm shells (OPS) to activated carbon (Microwave absorber), the temperature in the pyrolysis experiment, and the length of time it took for the experiment to obtain the maximum liquid product in this experiment The variables were controlled as follows:

1) Microwave pyrolysis system power 4,000 watts

2) Oil palm shells that had been crushed and sized to have a size of 1.18 - 2.00 mm.

3) Activated carbon that had been crushed and sized to have size 850 µm.

4) Determination of moisture content of palm shells, activated carbon ≤ 8 wt.%

5) Nitrogen flow rate at 1 LPM.

6) The ratio of oil palm shells to activated carbon was 70:30, 75:25, and 80:20.

7) The pyrolysis time was 30, 35, and 40 minutes.

8) The pyrolysis of temperature was 400, 550, and 700 degrees Celsius.

These controlled variables affect the product content, liquid, solid, gas, and chemical composition of bio-oil obtained from microwave pyrolysis.

**Part 2: Bio-phenol extraction by supercritical fluid with carbon dioxide process.**

The objective of the research is to study temperature and pressure for the experiment to obtain the maximum of bio-phenol the variables were controlled as follows:

1) The ratio of crude bio-oil (The maximum liquid yield from microwave pyrolysis) to Spe-ed Matrix (hydroscopic sample dispersing agent) was 2:1

2) Carbon dioxide flow rate at 3 LPM.

3) The extraction time was 30 minutes.

4) The extraction of temperature was 50, 60, and 70 degrees Celsius the extraction of pressure 300, 350, and 400 bar.

These controlled variables affect the product content and chemical composition of $scCO_2$ oil such as bio-phenol obtained from supercritical fluid extraction with carbon dioxide.

## 3.4 Experimental diagram of a microwave pyrolysis process

This research to study the ratio of oil palm shells (OPS) to activated carbon, the temperature in the pyrolysis experiment, and the length of time it took for the experiment to obtain the maximum liquid product which has the following study plans details in Figure 3.1

```
┌─────────────────────────────────────────────────────────────┐
│     Design of experiment for the microwave pyrolysis process. │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│          Calibration of microwave pyrolysis system            │
└─────────────────────────────────────────────────────────────┘
```

**Oil palm shell (OPS)**
- Preparation
1) Size around 1.18-2.0 mm.
2) Moisture content around 8 % wt.
- Analysis
1) Chemical properties by proximate and ultimate analysis

**Activated carbon (AC)**
- Preparation
1) Size around ≤ 850 μm.

2) Moisture content around 8 % wt.
- Analysis
1) Chemical properties by proximate and ultimate analysis
2) Surface area and porosity (BET)

The total weight is 500 g with ratio of OPS:AC as 70:30, 75:25, and 80:20.

Microwave pyrolysis
- Pyrolysis conditions
1) Temperature in the reactor is 400, 550, and 700°C.
2) Pyrolysis time for 30,35, and 40 minutes
3) Nitrogen flow rate of 1.0 LPM.

Product yield analyzing

Gas
- Content

Liquid (Bio-oil)
- Content
- Moisture content
- Chemical compositions by GC-MS

Solid (Bio-char)
- Content
- Chemical properties by proximate and ultimate analysis
- Surface area and porosity (BET)

**Figure 3.1** Diagram of experiment microwave pyrolysis

### 3.4.1 Design of experimental microwave pyrolysis process using computer programs

In this step, the conceptual design is to create a prototype microwave pyrolysis process to produce bio-oil from biomass residues in the palm oil industry using the COMSOL MultiPhysics$^{TM}$ program to simulate images of microwaves inside the designed system. It is a simulation program that relies on computational principles according to numerical methodology (Finite element method; FEM) to calculate the displacement and standing wave generation of microwaves within the designed system.

### 3.4.2 Design an experiment of microwave pyrolysis using the Minitab program.

This research used a statistical program Minitab to assist in experiment design and to analyze experimental results. which used the full factorial experiment design for studying factor 2 levels ($2^k$ Full Factorial Design: $2^3$). It assists in designing experiments and conducting optimal condition analysis of the microwave pyrolysis process. The factors studied were pyrolysis of time (Time), oil palm shell to activated carbon ratio (OPS: AC ratio), and temperature of the pyrolysis process (Temperature) where every factor has 2 Levels of variables and added the mean value of the factor for analysis of results by calculating the percentage of the highest crude bio-oil content. can be shown in Table 3.1 and the experimental design was performed for 2 replicates all 18 runs were executed in randomized order, which can be shown in Table 3.2

**Table 3.1** Factor levels used in full factorial design

| Factor | Low (-1) | High (+1) |
|---|---|---|
| Temperature ($^o$C) [T] | 400 | 700 |
| OPS : AC [R] | 70:30 | 80:20 |
| Time (s) [t] | 30 | 40 |

**Table 3.2** The experimental design using the Minitab program, a randomized trial.

| Case | Temperature (°C) | The ratio of oil palm shells to activated carbon | Time in the pyrolysis process (minutes) |
|---|---|---|---|
| 1 | 700 | 80:20 | 30 |
| 2 | 700 | 80:20 | 30 |
| 3 | 700 | 70:30 | 30 |
| 4 | 700 | 70:30 | 30 |
| 5 | 700 | 80:20 | 40 |
| 6 | 700 | 80:20 | 40 |
| 7 | 700 | 70:30 | 40 |
| 8 | 700 | 70:30 | 40 |
| 9 | 550 | 75:25 | 35 |
| 10 | 550 | 75:25 | 35 |
| 11 | 400 | 80:20 | 30 |
| 12 | 400 | 80:20 | 30 |
| 13 | 400 | 70:30 | 30 |
| 14 | 400 | 70:30 | 30 |
| 15 | 400 | 80:20 | 40 |
| 16 | 400 | 80:20 | 40 |
| 17 | 400 | 70:30 | 40 |
| 18 | 400 | 70:30 | 40 |

### 3.4.3 The preliminary test of the microwave pyrolysis system with water

The preliminary work of the microwave pyrolysis system using water as a calibration power of the microwave system. The system used in the experiment is shown in Figure 3.2
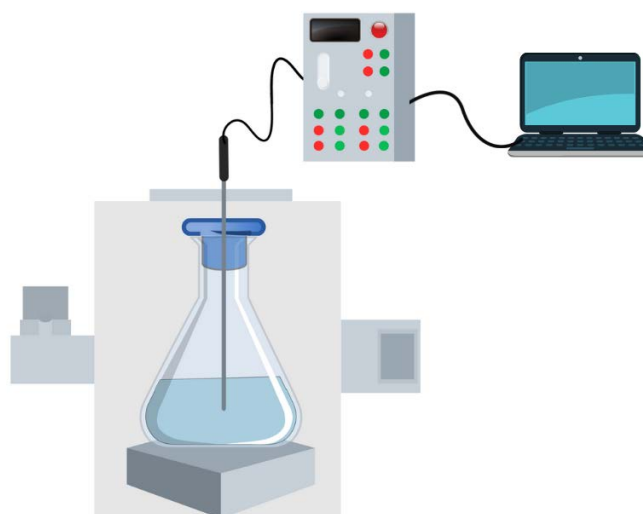
**Figure 3.2** Preliminary testing of Microwave pyrolysis system used to water.

Testing the microwave pyrolysis system using a volume of water 500 ml filled in a quartz reactor the temperature control to 80 ± 2 °C for 5 minutes to test microwave pyrolysis and temperature control systems. The picture of the top view shows the location of the installation of the 1-4 magnetron as shown in Figure 3.3
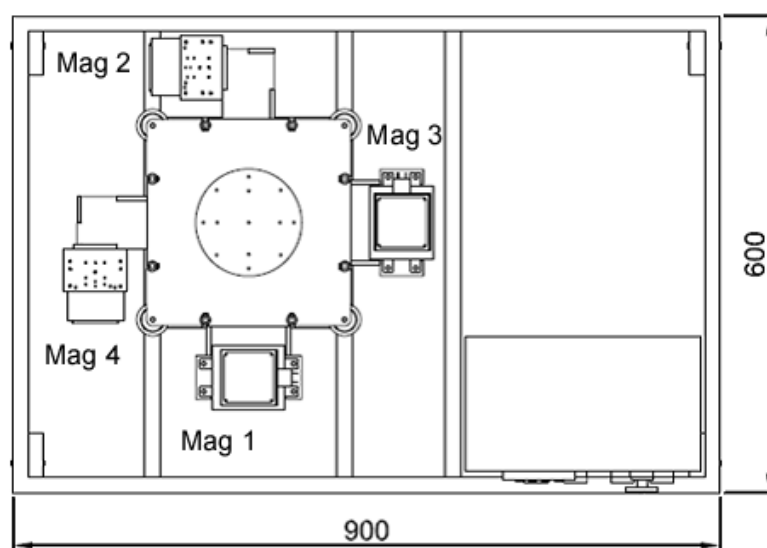


**Figure 3.3** The installation of magnetrons 1 to 4 (Mag 1234) of the microwave pyrolysis system.

The test of microwave pyrolysis using water consisted of 3 cases as follows:

1) Using a volume of water 500 ml filled in a quartz reactor control the temperature of water to $80 \pm 2$ °C for 5 minutes and use power from the $1^{st}$ magnetron (Mag 1) and the $2^{nd}$ magnetron (Mag 2); (Mag 1-2).

2) Using a volume of water 500 ml filled in a quartz reactor control temperature of water to $80 \pm 2$ °C for 5 minutes and use power from the $3^{rd}$ magnetron (Mag 3) and the $4^{th}$ magnetron (Mag 4); (Mag 3-4).

3) Using a volume of water 500 ml filled in a quartz reactor control temperature of water to $80 \pm 2$ °C for 5 minutes and use power from $1^{st}$ magnetron (Mag 1), $2^{nd}$ magnetron (Mag 2), $3^{rd}$ magnetron (Mag 3) and $4^{th}$ magnetron (Mag 4); (Mag 1,2,3, and 4)

### 3.4.4 The preliminary test of the microwave pyrolysis system with test material

In this step, The preliminary test of the microwave pyrolysis process with the test material. This makes it know the microwave power of the magnetron for each pair and all the magnetrons. The materials tested in the research include oil palm shells (OPS), activated carbon (AC) commercial grade. Preparing a microwave pyrolysis system is shown in Figure 3.4
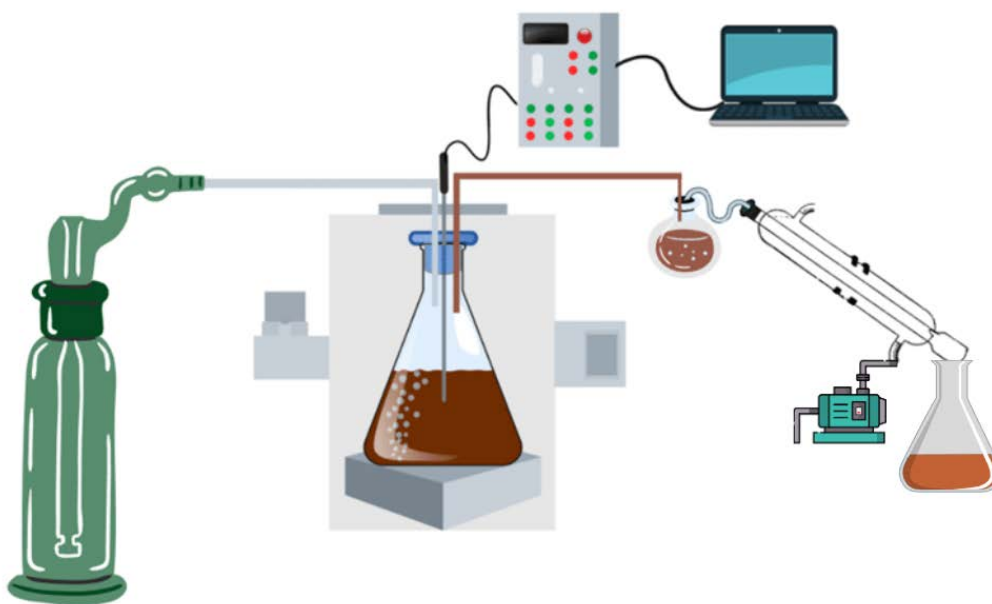


**Figure 3.4** The preliminary testing of the microwave pyrolysis system with test material

The microwave pyrolysis system was tested with the test material as follows:

1)   The ratio of oil palm shell to activated carbon is 70:30 with the total weight of the material 500 grams the flow rate of nitrogen gas is 4 LPM. the pyrolysis time is 35 minutes were used Magnetrons 1 and 2 were as test samples and controlled the pyrolysis temperature at 400 °C.

2)   The ratio of oil palm shell to activated carbon is 70:30 with the total weight of material 500 grams. The flow rate of nitrogen gas is 4 LPM. The pyrolysis time is 35 minutes. were used Magnetrons 1234 as a test sample controlled the pyrolysis temperature at 700 °C.

**3.4.5 Preparation of raw materials used in the microwave pyrolysis process.**

1)   Preparation of oil palm shell

Oil palm shells (OPS) are courtesy of The Southern Palm (1978) Co., Ltd. which is a company Crude palm oil industry group in Surat Thani Province. Preparation of raw materials by crushing and screening oil palm shells to a size of 1.18 mm (Sieve No. 16) to 2.00 mm. (Sieve No. 10), after that, it is dried in a hot air oven at 105 °C to reduce the moisture content to less than 8% wt.

2)   Preparation of activated carbon (Microwave absorber)

The activated carbon is a commercial grade made from coconut shells as a microwave absorber in this research. Preparation of raw materials by crushing and screening activated carbon to a size of ≤ 850 μm (Sieve No.20) after that, it is dried in a hot air oven at 105 °C to reduce the moisture content to less than 8% wt. Then, the material that has been screened and reduced moisture content to less than 8 %wt. is packed into a zip-lock plastic bag to maintain the moisture content of the raw material.

**3.4.6 Experiment to determine the optimum conditions of crude bio-oil production by microwave pyrolysis system**

The experiment in the microwave pyrolysis process involves the following steps:

1)    The test material prepared, was an oil palm shell to activated carbon were mixed according to the ratio of each experiment as shown in Table 3.2 the total weight of the test material for all experiments was 500 grams and then loaded into the quartz reactor as shown in Figure 3.5 (a) then close the quartz reactor with insulated Teflon. The quartz reactor was placed in a microwave oven (cavity) as shown in Figure 3.5 (b).



(a)                                                           (b)

**Figure 3.5** (a) Packing of test material in quartz reactor (b) filling the quartz reactor in the microwave (cavity)

2)    After place the quartz reactor in a cavity and close it with a stainless-steel lid tightly to prevent microwave leakage during the experiment before the start of the microwave pyrolysis process, the oxygen gas must be replaced so that it does not ignite inside the microwave pyrolysis system with the release of nitrogen gas ($N_2$) which is an inert gas into the system determining the flow rate of nitrogen gas is 1 LPM. into the system for 5 minutes before the microwave pyrolysis system was turned on to heat the test material for a specified time after the pyrolysis is complete must be released $N_2$ in the system for another 3 minutes to dissipate the heat contained in the

system and collect liquid products both parts are obtained from the condensation system. The microwave pyrolysis system is shown in Figure 3.6



**Figure 3.6** The experiment of microwave pyrolysis system

During the first 10 minutes of the experiment, the temperature of the test material was rapidly increased, and a large amount of gas will be observed flowing into the condensation system as shown in the Figure 3.7 The gas is obtained from the microwave pyrolysis system at very high temperatures it flows into condensation system, it results in the condensation of gas to liquid.
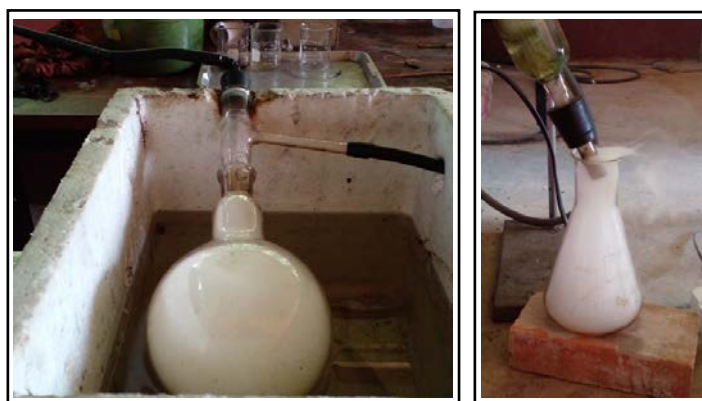


**Figure 3.7** Condensation of gas from a microwave pyrolysis system

3) The experiment complete, the liquid product (bio-oil) form microwave pyrolysis process obtained in the round-bottom flask and spiral condensation systems. The bio-oil collected in the two containers was then poured

together to measure the amount of crude bio-oil produced and the solid products in quartz reactor.

      4)   The products obtained from the microwave pyrolysis process were analyzed for properties. Liquid product (bio-oil) and solid product (Bio-char) with the methods and analytical tools as detailed in Table 3.3

**Table 3.3** Methods for analyzing properties and crude bio-oil and bio-char products obtained from microwave pyrolysis.

| Product | feature | Testing Methods/Testing Tools |
|---------|---------|-------------------------------|
| Crude bio-oil | chemical composition | Gas Chromatograph-Mass Spectrometer (GC-MS) |
| Bio-char | Surface physical properties Average pore diameter pore volume | Braeuer-Emmett-Teller (BET) |
| | morphology surface conditions | Scanning Electron Microscope (SEM) |
| | Heating value | Bomb calorimeter |

      **3.4.7 Experimental diagram of bio-phenol extraction from crude bio-oil by supercritical fluid extraction with carbon dioxide**

      This research to study bio-phenol extracted from crude bio-oil by supercritical extraction with carbon dioxide, the temperature, pressure, the extraction time, and carbon dioxide gas with flow rate for the experiment to obtain the maximum of bio phenol which has the following study plans details in Figure 3.8

Design of experiment for the extracted bio-phenol by supercritical fluid extraction with carbon dioxide.

Crude bio-oil from microwave pyrolysis for the optimum condition from part 1.

The ratio of crude bio-oil: spe-ed matrix seed as 2:1 (20 g of total weight).

Supercritical fluid extraction with carbon dioxide.

1) Temperature as 50, 60, and 70 °C.

2) Pressure as 300, 350, and 400 bar.

3) Extraction time as 30 minutes.

4) Carbon dioxide gas with a flow rate of 3.0 LPM.

Product yield ($scCO_2$ oil) analyzing.

-   Chemical compositions by GC-MS

Cost estimation of bio-phenol production.

**Figure 3.8** Diagram of Bio-phenol extraction by supercritical fluid extraction with carbon dioxide

### 3.4.8 Experiment to bio-phenol extraction from crude bio-oil by supercritical fluid extraction with carbon dioxide

Bio-oil obtained from microwave pyrolysis was extracted bio-phenol by supercritical fluid extraction with carbon dioxide ($scCO_2$) process which is the process that puts carbon dioxide in a supercritical fluid state. This is the process that puts carbon dioxide into a supercritical liquid state. Supercritical carbon dioxide has a temperature of 31 °C and a pressure of 73.8 bar as shown in Figure 3.9
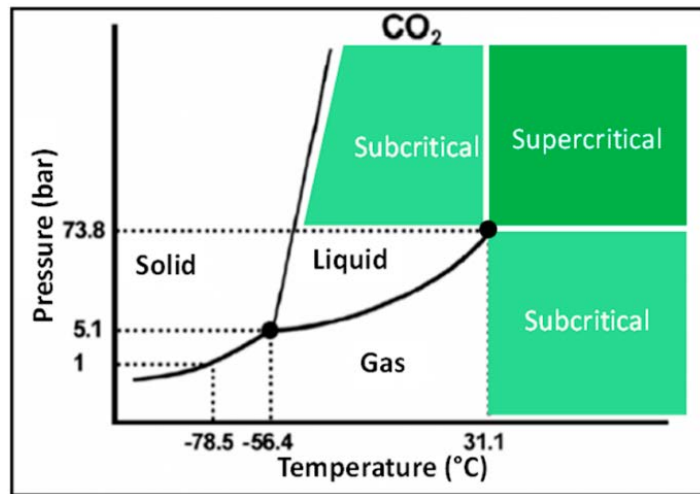
**Figure 3.9** Correlation between temperature and pressure that affect various states of carbon dioxide (Laboureur, Ollero, & Touboul, 2015)

This research project used the Applied Separations Spe-ed$^{TM}$ SFE-4 extractor. The features of the machine can be set for pressure up to 689.476 bar (10,000psi) and a temperature of 240 °C. The characteristics of the front and back of the machine are shown in Figure 3.10 and 3.11 respectively.
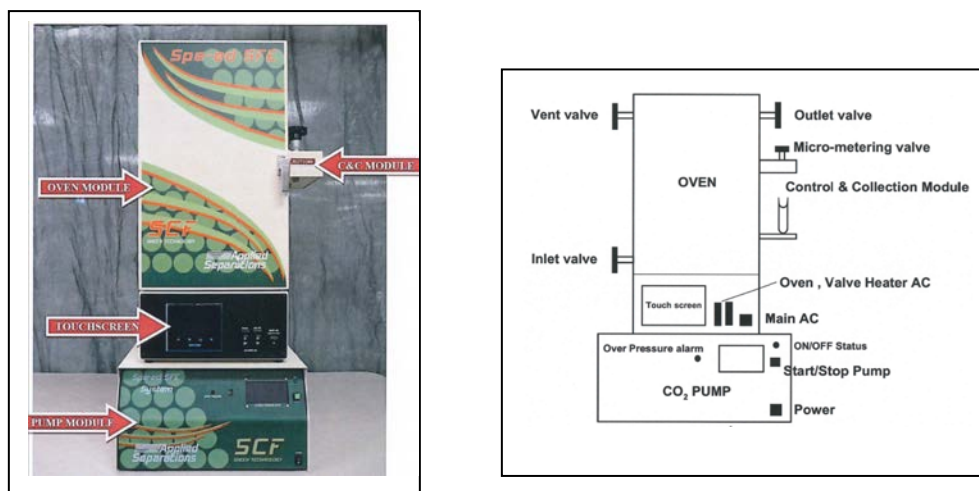


**Figure 3.10** The extractor and its components show the front view of the machine scCO$_2$ model *Spe-ed$^{TM}$* SFE-4.
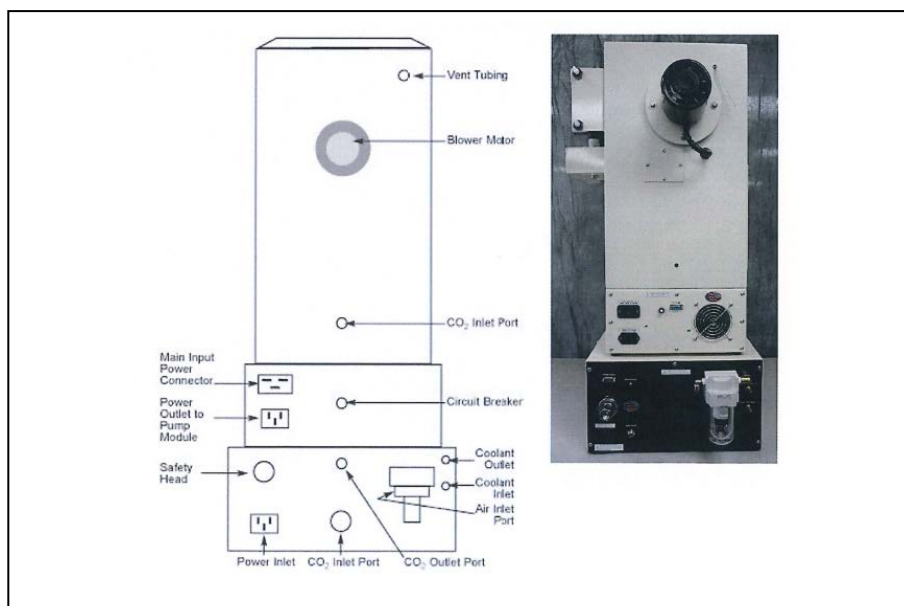
**Figure 3.11** The extractor and components show a back view of the *Spe-ed$^{TM}$* SFE-4 scCO$_2$.

3.4.8.1 Design an experiment of supercritical fluid extraction with carbon dioxide

This research investigated the experimental design of the bio-phenol extraction process using a supercritical critical fluid with carbon dioxide process. The factor studied was the temperature of the extraction process and the pressure of the extraction process at all factors having 2 variable levels as shown in Table 3.4 and increasing the mean of the factors and experimental design two replicates randomly assigned to the experiment as shown in Table 3.5

**Table 3.4** The levels of factor used in the design

| Factor | Low (-1) | High (+1) |
|---|---|---|
| Temperature ($^{o}$C) [T] | 50 | 70 |
| Pressure (bar)[P] | 300 | 400 |

**Table 3.5** Bio-phenol extraction experimental design.

| Case | Conditions | | | |
|---|---|---|---|---|
| | **Temperature(ºC)** | **Pressure (bar)** | **Time (minute)** | **Flow rate of $CO_2$ (LPM.)** |
| 1 | 50 | 300 | 30 | 3.0 |
| 2 | 50 | 400 | 30 | 3.0 |
| 3 | 60 | 350 | 30 | 3.0 |
| 4 | 70 | 300 | 30 | 3.0 |
| 5 | 70 | 400 | 30 | 3.0 |
| 6 | 50 | 300 | 30 | 3.0 |
| 7 | 50 | 400 | 30 | 3.0 |
| 8 | 60 | 350 | 30 | 3.0 |
| 9 | 70 | 300 | 30 | 3.0 |
| 10 | 70 | 400 | 30 | 3.0 |

        3.4.8.2 Method of the experiment of supercritical fluid extraction with carbon dioxide process

        The experiment of supercritical fluid extraction with carbon dioxide process involves the following steps:

        1) Preparation of materials for bio-phenol extraction testing from crude bio-oil

        The experiment was initiated by using the crude bio-oil obtained from the microwave pyrolysis process shown in Figure 3.12 (a) in which the samples are thick and sticky by bringing crude bio-oil mixed with hydroscopic sample dispersing agent (Spe-ed Matrix seed) which looks solid lightweight, like a small foam as shown in Figure 3.12 (b) the ratio of crude bio-oil to hydroscopic sample dispersing agent is 2:1. It absorbs crude bio-oil and increases the surface area in the $scCO_2$ process and mixtures of crude bio-oil and hydroscopic sample dispersing agents can be shown in Figure 3.12 (c).
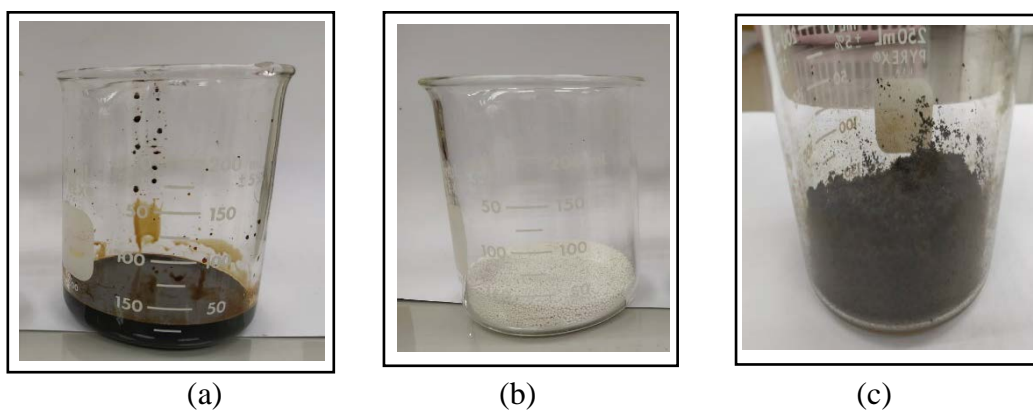
**Figure 3.12** (a) Characteristics of crude bio-oil (b) Characteristics of Spe-ed Matrix
(c) Composites of Crude Bio-oil and hydroscopic sample dispersing agent
of $scCO_2$

2) Packing of mixtures of crude bio-oil and hydroscopic sample dispersing agent bio-oil amount of 10 grams into the vessel and load the vessel in the machine supercritical fluid extraction as shown in Figure 3.13
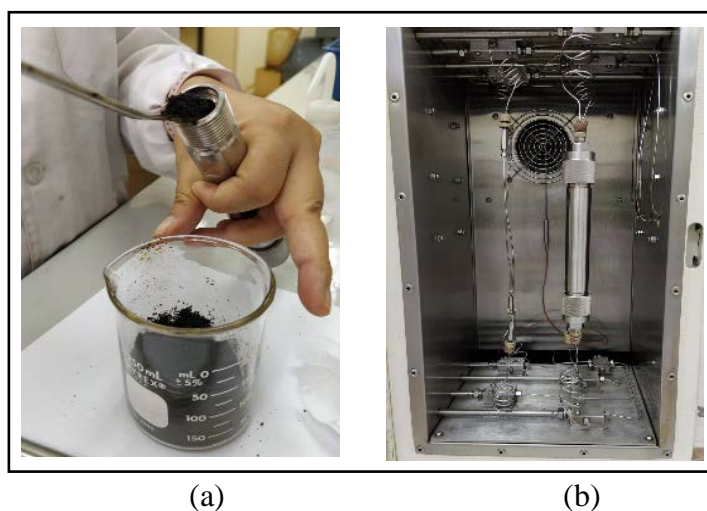


**Figure 3.13** (a) Loading of sample material for $scCO_2$ test into the vessel

(b) Loading into the vessel in $scCO_2$ extractor.

3) Temperature and pressure were adjusted according to the specified conditions as shown in Table 3.3 and using a flow rate of carbon dioxide are 3 LPM. for a while is 30 minutes in the supercritical fluid extraction with carbon

dioxide process which is a solvent flows through the sample material for testing throughout the extraction period without leaving the solvent soaked. It is continuous extraction throughout the extraction period.

# CHAPTER 4

# RESULTS AND DISCUSSION

The objective of the research is to study the influence of parameters such as the ratio of OPS to MWAb, and pyrolysis temperature. The liquid yield is obtained from the microwave pyrolysis process, in addition, this research examines the temperature, pressure, and yield from the supercritical fluid process with carbon dioxide and the chemical composition of oils extracted from the supercritical fluid process with carbon dioxide. Therefore, the results of the experiments were shown, and the results were discussed as follows.

## 4.1 Concept and method of development of microwave pyrolysis system for crude bio-oil and bio-char production from biomass residues in the crude palm oil industry

### 4.1.1 Microwave oven (cavity)

The microwave oven (cavity) consists of 4 magnetrons (microwave source). The microwave oven is made of stainless steel, size is 0.22x0.22x0.31 m. The results of the wave dispersion simulation. microwave in the oven with the COMSOL Multiphysics$^{TM}$ program the finite element method (FEM) could be shown in Figure 4.1, where the red position indicates the position at which the microwave wave has the highest reinforcement intensity according to the scale of the band as shown in the figure on the side of the model.
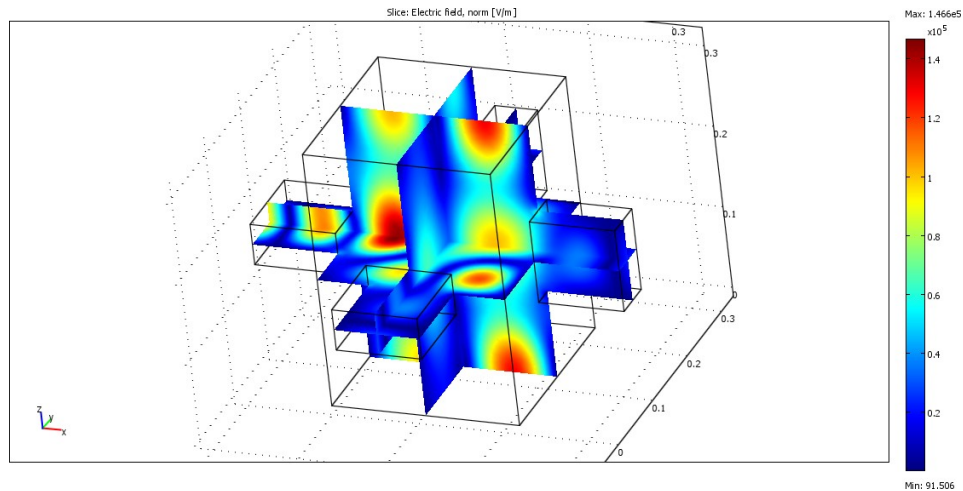
**Figure 4.1** Microwave electric field simulation in a microwave pyrolysis system using the Comsol MultiPhysics<sup>TM</sup> program

Design and simulation distribution of microwave waves inside the cavity shows the distribution waves inside a microwave oven, especially in the middle position where the quartz reactor is placed that is packed OPS inside to create an interaction between microwave and OPS until heat. Subsequently, a microwave pyrolysis system was created according to the size obtained to perform simulations with computer programs Figure 4.2 shows the design of the microwave system with a computer in three dimensions and Figure 4.3 shows an overview of the components system to be built.
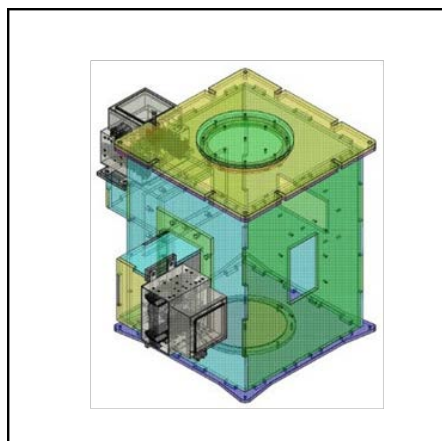


**Figure 4.2** Three-dimensional model of the microwave pyrolysis system with a computer program
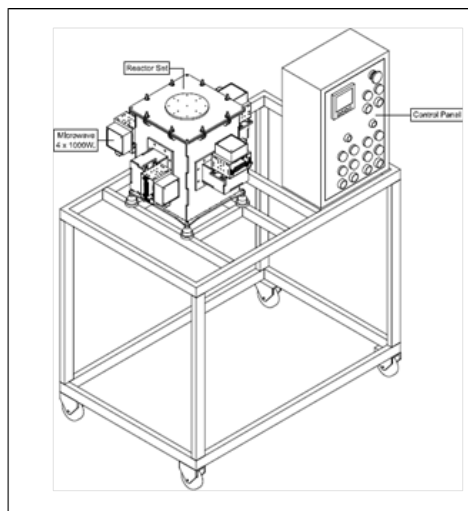
**Figure 4.3** The reactor of microwave pyrolysis system for the production of bio-oil and bio-char that are designed and proceeded to create.

The microwave oven (cavity) is used for packing quartz reactor, which is in the shape of an Erlenmeyer flask. The mouth of the bottle has a diameter of 5.0 cm, the bottom of the bottle has a diameter of 16.0 cm, and the height is 26.5 cm. The lid of the quartz reactor is teflon material. The microwave oven lid is made of stainless steel and the Teflon lid (quartz reactor lid) is punched in 3 holes. The first compartment is used for feeding nitrogen gas into the system, the second compartment is used to install the thermocouple, and the third compartment is used as an exit for the gas to enter the condensation system further.

### 4.1.2 Temperature control system

The microwave pyrolysis system controls the temperature by using the Digital Temperature Controller brand SHIMAX Model MAC3D-MSF-ES-NRN body size 48x48 mm. The input that can be used is a thermocouple (K, J, T, E, R, S, U, N, B, Pr/RTD PT100/JPt 100. The voltage is 0-10 mV, 0-20 mV, -10-10 mV, 0-50 mV, and 0-100 mV and has two outputs, which are pulsed driving a solid-state relay 12VDC 20 mA. The temperature can be sent and recorded to the computer via the RS485 device while experimenting in real-time, which is used in conjunction with the Shimax Soft program start the temperature control system by installing a thermocouple type K to measure the temperature in a microwave pyrolysis system. The digital temperature controller amplifies the signal from the thermocouple and reads the temperature to be

able to control the temperature to 400, 550, and 700 degrees Celsius and install a Solid State Relay (SSR) which acts as a circuit breaker switch by using electromagnets as a switch to turn on and off microwave energy. The temperature control during the experiment must be able to achieve the maximum and minimum temperature settings quickly and continuously.

### 4.1.3 Condensation system

The condensation system used has two steps: The first step was a condensing system that uses a round bottom flask to accommodate fast condensing liquid products and the second step was a condensing system using a condenser unit bulb (Allihn Condenser) to accommodate slow condensation liquid products. Both steps have a water pump system that circulates the coolant to reduce the temperature of the product and control the coolant temperature to be in the range of 3-5 degrees celsius by using a temperature data logger, DIGICON brand, model DP.745D.

### 4.1.4 Watt-hour meter system

The Power Meter brand KEPLER model Alianze Energy Pro was used in this research. The electric energy meter is a device that displays the parameters and quantities of various electrical energy such as voltage, current, actual power, reactive power, etc. To know the electricity cost in the production process of using electricity to control or improve the use of electricity to achieve full efficiency of work, as well as to help manage energy. In research, the program Alianze Energy Pro was used to control the use of the energy meter during experiments.

The results of the process for the development of a microwave pyrolysis system for the production of bio-char and bio-oil for the extraction of bio-phenol by the supercritical fluid process which has been installed microwave power system (Magnetron) 4 units conjunction with ventilation system consisting of fans on stainless steel reactors to form an interaction zone between the microwave and palm shells for the microwave pyrolysis process including the electrical control cabinet that powers the magnetron to convert electrical energy to microwave energy with watt-hour meter are an indicator of the power consumption of the system, including installing temperature control and ventilation systems in addition to the above-mentioned systems. The whole

system is built on a stainless-steel structure supported by wheelbases for ease of work, testing, and moving installation.

**4.1.5 Microwave pyrolysis system for producing crude bio-oil and bio-char from biomass residues in the crude palm oil industry that have been created**

The design concept and method of development of microwave pyrolysis system for bio-oil and bio-char from biomass residues in the crude palm oil industry as mentioned above, enabling the creation of a prototype microwave pyrolysis system as shown in Figure 4.4



**Figure 4.4** Prototype microwave pyrolysis system for producing crude bio-oil and bio-char

**4.2 The results of the preliminary test microwave pyrolysis system testing with water.**

The results of the preliminary test of the microwave pyrolysis system using 500 ml of water as a calibration microwave power of the pyrolysis microwave system are shown in Figure 4.5.
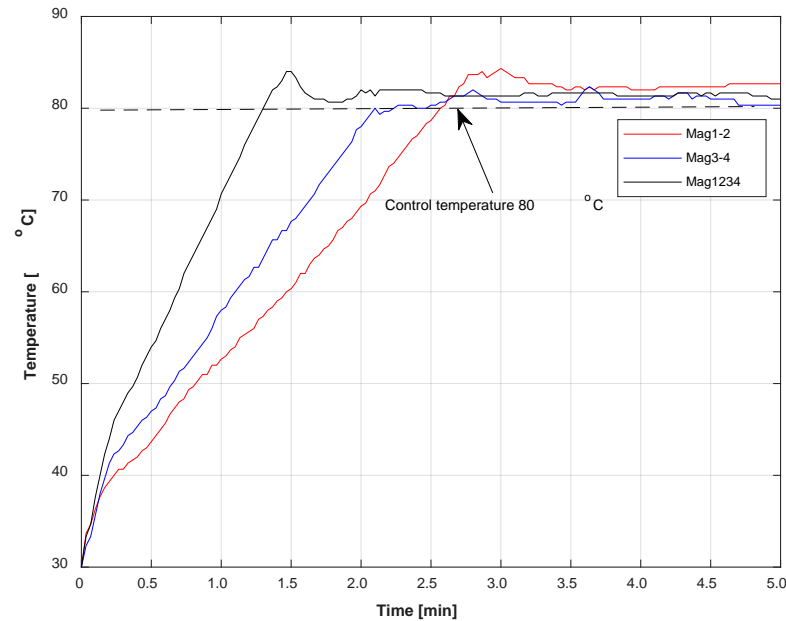


**Figure 4.5** The time profiles of temperature from system calibrations using 500 ml of water.

It can determine the microwave power generated by the magnetron in different positions by calculating the power (P) of the heat-converting microwave wave from Equation:

$$P(Watt) = \frac{4.19 \times V \times \Delta T}{t} \qquad (4.1)$$

Where V is the volume in milliliters.

ΔT is the temperature change in degrees Celsius and

t is the time in seconds

Therefore, to determine the microwave power of the generated pyrolysis microwave system, the system power was calculated according to equation 4.1 and the calculation time was taken for 1 minute pyrolysis can be shown in Table 4.1.

**Table 4.1** Microwave power is calculated from microwave pyrolysis systems at different magnetron positions.

| Case | Position of magnetron | The preliminary temperature of the water $T_0$ (ºC) | The final temperature of the water $T$ (ºC) | Temperature different $\Delta T = T - T_0$ ℃ | Power of microwave system $P(Watt)$ |
|------|------------------------|-------------------------------------------------|-----------------------------------------|------------------------------------------|----------------------------------|
| 1 | Mag 1-2 | 30.0 | 53.0 | 23.0 | 803.1 |
| 2 | Mag 3-4 | 30.0 | 58.3 | 28.3 | 989.3 |
| 3 | Mag 1-4 | 30.0 | 71.1 | 41.7 | 1,454.9 |

The results in the table showed that when testing the microwave power of the system by turning on magnetron positions 1 and 2 the microwave power of the system was 803.1 Watts. When magnetron positions 3 and 4 were turned on the microwave power of the system was 989.3 Watts. However, in the calibration all four magnetrons Mag1234 received the Microwave power 1,454.9 Watts.

**4.3 The result of the preliminary test of microwave pyrolysis system by oil palm shell.**

The preliminary test of the microwave pyrolysis system by testing with palm shell and activated carbon commercial grade. The effect of temperature change inside the reactor versus time is shown in Figure 4.6
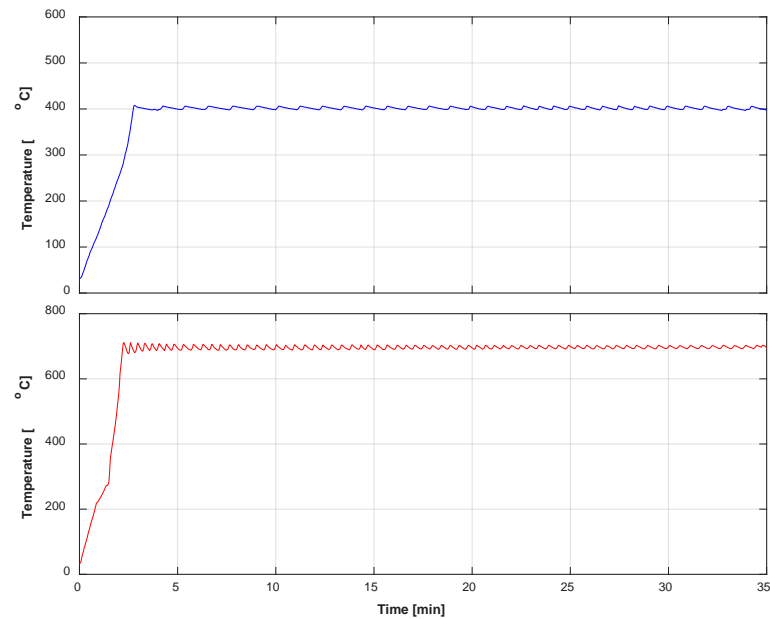
**Figure 4.6.** The temperature change compared to the time of the microwave pyrolysis virtual experiment.

The top picture-blue curve is the result of 3.3.1 and the bottom-red curve is the result of 3.3.2

a) The ratio of oil palm shell to activated carbon (OPS: AC) = 70:30 and using magnetrons 1 and 2

b) The ratio of oil palm shell to activated carbon (OPS: AC) = 70:30 and using magnetron at 3 and 4.

The temperature change over time of the 35 min microwave pyrolysis virtual experiment can be shown in Figure 4.6. The above figure - the blue curve is a virtual experiment with the condition the ratio of experimental material OPS: AC was 70:30 by total weight equal to 500 g, the flow rate of nitrogen gas 4 liters/minute. The pyrolysis time is 35 minutes magnetrons 1 and 2 were used as the test samples and the pyrolysis temperature was controlled at 400°C. It was found that the system was able to adjust the temperature of the experimental material from room temperature to a controlled temperature of 400 °C in 3 minutes and the microwave power control system works in the control by showing through the temperature of the experimental material in the manner of temperature fluctuations up and down. The temperature cycle is well controlled. The product obtained from the microwave pyrolysis system in the solid

phase of 398 g, the liquid of 45 g, and the gas (non-condensable gas) of 57 g. The figure of the product obtained from the virtual experiment for solid and liquid phase products can be shown in Figure 4.7 and Figure 4.8 a) respectively. The temperature variations up and down control at a temperature of 700 °C. It was as good as a virtual experiment of microwave pyrolysis at a temperature of 400 °C but the material temperature rises from room temperature to the controlled temperature very quickly in just 2.5 minutes. The product was obtained from a microwave pyrolysis system in a solid phase of 356 g, a liquid of 59 g, and a gas (non-condensable gas) of 85 g. The Figure of the product obtained from the experiment for solid and liquid products can be seen in Figure 4.7. and Figure 4.8 b) respectively.



**Figure 4.7** Solid product (bio-char) obtained by microwave pyrolysis.
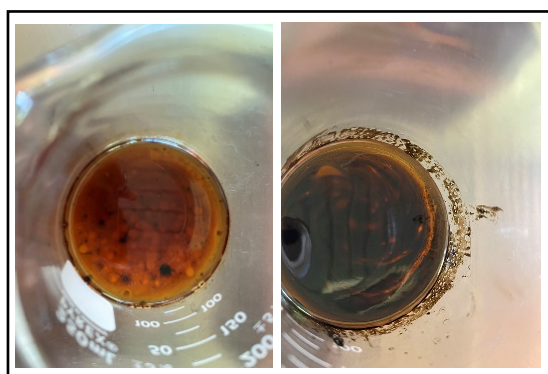


**Figure 4.8** Liquid product (Crude bio-oil) obtained from microwave pyrolysis
a) Conditional virtual experiments temperature at 400 °C and
b) Obtained from conditional virtual experiments temperature at 700 °C

**4.4 The results of the experiment to determine the optimum conditions for bio-oil production with the developed microwave pyrolysis system.**

The experiment has been designed of experiment with the method of $2^k$ Full Factorial Design: $2^3$ with three factors. The second level and the test at the mean level are shown in Table 3.4, and Table 3.1. The results are shown in Table 4.2.

**Table 4.2** Product of the microwave pyrolysis process.

| Case | Temp (ºC) | Ratio | Time (min) | Bio-oil (ml) | % Yield | | |
|------|-----------|-------|------------|--------------|---------|--------|------|
| | | | | | solid | liquid | gas |
| 1 | 700 | 80:20 | 30 | 116 | 45.6 | 23.2 | 31.2 |
| 2 | 700 | 70:30 | 40 | 94 | 53.2 | 18.8 | 28.0 |
| 3 | 700 | 70:30 | 30 | 95 | 49.4 | 19.0 | 31.6 |
| 4 | 700 | 80:20 | 30 | 107 | 43.0 | 21.4 | 35.6 |
| 5 | 700 | 70:30 | 40 | 98 | 56.8 | 19.6 | 23.6 |
| 6 | 700 | 70:30 | 30 | 112 | 54.0 | 22.4 | 23.6 |
| 7 | 400 | 80:20 | 30 | 31 | 79.0 | 6.2 | 14.8 |
| 8 | 400 | 80:20 | 30 | 33 | 81.8 | 6.6 | 11.6 |
| 9 | 400 | 70:30 | 40 | 33 | 77.0 | 6.6 | 16.4 |
| 10 | 400 | 70:30 | 30 | 48 | 81.2 | 9.6 | 9.2 |
| 11 | 400 | 80:20 | 40 | 56 | 79.8 | 11.2 | 9.0 |
| 12 | 400 | 70:30 | 30 | 44 | 43 | 21.4 | 35.6 |
| 13 | 700 | 80:20 | 40 | 123 | 53.2 | 24.6 | 22.2 |
| 14 | 550 | 75:25 | 35 | 88 | 53 | 16.8 | 30.2 |
| 15 | 400 | 80:20 | 40 | 48 | 83 | 9.6 | 7.4 |
| 16 | 550 | 75:25 | 35 | 84 | 53.2 | 17.6 | 29.2 |
| 17 | 700 | 80:20 | 40 | 116 | 54.8 | 23.2 | 22.0 |
| 18 | 400 | 70:30 | 40 | 30 | 59.4 | 6.0 | 34.6 |

The analysis of variance, the factorial regression results for the product percentage (%yield), the liquid phase, and all three factors, the model summary, the coded coefficients, and Regression Equation in Uncoded Units as shown in Equation 4.2 with a 95% confidence interval test using a computer program. The results of the analysis are shown in Table 4.3.

**Table 4.3** Factorial regression ANOVA for the liquid phase product percentage with all three factors using a computer program.

Factorial Regression: %Yield versus Temp, Ratio, Time

| Source | DF | Adj SS | Adj MS | F-Value | P-Value |
|---|---|---|---|---|---|
| Model | 7 | 708.150 | 101.164 | 12.23 | 0.000 |
| Linear | 3 | 578.750 | 192.917 | 23.32 | 0.000 |
| Temp | 1 | 571.210 | 571.210 | 69.05 | 0.000 |
| Ratio | 1 | 0.250 | 0.250 | 0.03 | 0.865 |
| time | 1 | 7.290 | 7.290 | 0.88 | 0.370 |
| 2-Way Interactions | 3 | 105.390 | 35.130 | 4.25 | 0.035 |
| Temp*Ratio | 1 | 30.250 | 30.250 | 3.66 | 0.085 |
| Temp*time | 1 | 6.250 | 6.250 | 0.76 | 0.405 |
| Ratio*time | 1 | 98.890 | 68.890 | 8.33 | 0.016 |
| 3-Way Interactions | 1 | 24.010 | 24.010 | 2.90 | 0.119 |
| Temp*Ratio*time | 1 | 24.010 | 24.010 | 2.90 | 0.119 |
| Error | 10 | 82.730 | 8.273 | | |
| Curvature | 1 | 4.410 | 4.410 | 0.51 | 0.495 |
| Pure Error | 9 | 78.320 | 8.702 | | |
| Total | 17 | 790.880 | | | |

Model Summary

| S | R-sq | R-sq(adj) | R-sq(pred) |
|---|---|---|---|
| 2.87628 | 89.54% | 82.22% | 60.78% |

Coded Coefficients

| Term | Effect | Coef | SE Coef | T-Value | P-Value | VIEW |
|---|---|---|---|---|---|---|
| Constant | | 15.800 | 0.678 | 23.31 | 0.000 | |
| Temp | 11.950 | 5.975 | 0.719 | 8.31 | 0.000 | 1.00 |
| Ratio | 0.250 | 0.125 | 0.719 | 0.17 | 0.865 | 1.00 |
| Time | -1.350 | -0.675 | 0.719 | -0.94 | 0.370 | 1. 00 |
| Temp*Ratio | 2.750 | 1.375 | 0.719 | 1.91 | 0.085 | 1.00 |
| Temp*Time | 1.250 | 0.625 | 0.719 | 0.87 | 0.405 | 1.00 |
| Ratio*Time | 4.150 | 2.075 | 0.719 | 2.89 | 0.016 | 1.00 |
| Temp*Ratio*Time | -2.450 | -1.225 | 0.719 | -1.70 | 0.119 | 1.00 |

Regression Equation in Uncoded Units

$$\% \text{Yield} = 778 - 0.984\ Temp - 10.18\ Ratio - 20.29\ Time + 0.01327\ Temp*Ratio + 0.0253\ Temp*Time + 0.263\ Ratio*Time - 0.000327\ Temp*Ratio*Time \quad (4.2)$$

Each factor was analyzed using P-Value statistical values at 95% confidence intervals. P-Value < 0.05 indicates that the factors or variables considered significantly affect the %yield response of bio-oil. Conversely, if the P-Value ≥ 0.05 that factor does not significantly contribute to the %yield of bio-oil. From Table 4.3, the P-Value of curvature (0.495) is greater than 0.05, indicating that the equation model The regression of equation (4.2) with the calculated correlation can be used, and when considering the summary of the model, the correlation coefficient (R-sq = $R^2$) is 89.54% and the improvement correlation coefficient (R-sq (adj) = $R^2$(adj) is 82.22%, which is greater than 70% acceptable. When performing residual analysis as shown in Figure 4.9, it was found that the error value had a normal distribution. The error values were distributed in a normal probability plot and histogram format. The error values were uniform when validated with versus fits of the error and found that the error data There is a versus order.
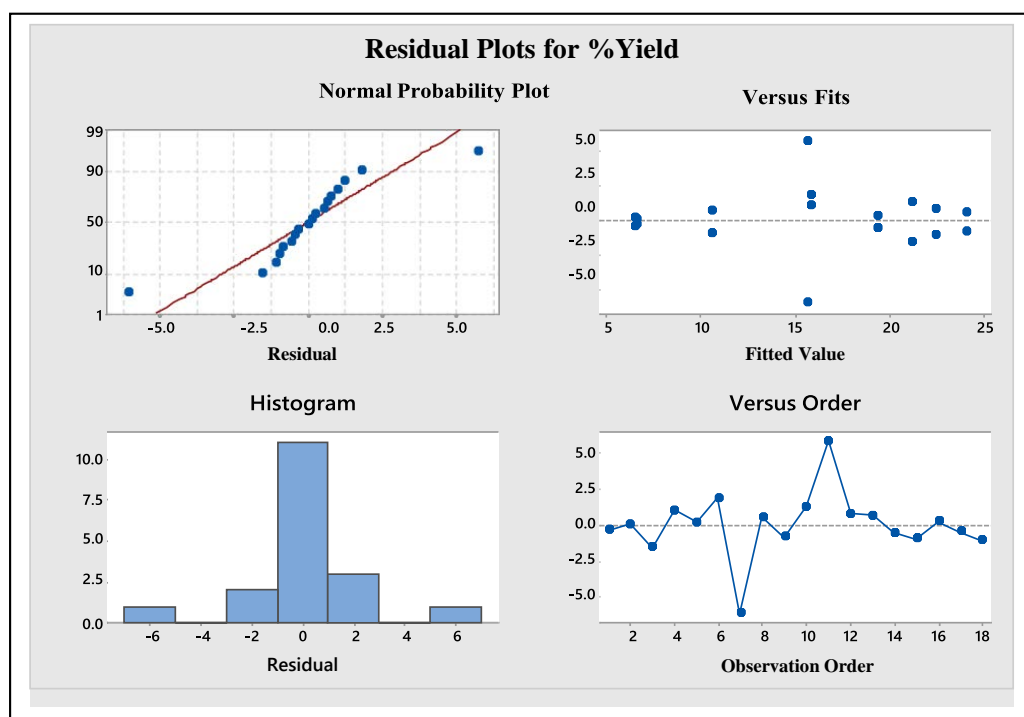


**Figure 4.9** The results of residual analysis

From the above data, it is shown that Equation 4.2 is suitable for predicting the percentage yield of bio-oil. Therefore, with the ability of a computer program, Equation 4.1 was used to find the optimum point of the response, the % yield

of bio-oil. To determine the response with maximize, the analysis results are shown in Table 4.4 and Figure 4.10

**Table 4.4** The results of optimum point analysis of the maximum yield of bio-oil content by a statistical program

Response Optimization: %Yield Parameters

| Response | Goal | Lower | Target | Upper | Weight | Importance |
|---|---|---|---|---|---|---|
| %Yield | Maximum | 6 | 24.6 | | 1 | 1 |

Solution and Multiple Response Prediction

| Solution | Temp | Ratio | Time | %Yield Fit | Composite Desirability |
|---|---|---|---|---|---|
| 1 | 700 | 80 | 40 | 24.075 | 0.971774 |

| Response | Fit | SE Fit | 95% CI | 95% PI |
|---|---|---|---|---|
| %Yield | 24.07 | 2.02 | (19.57, 28.58) | (16.24, 31.91) |
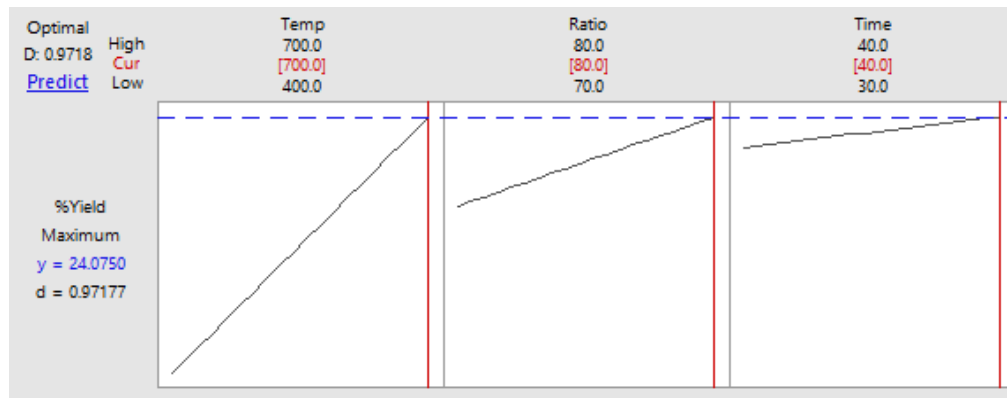


**Figure 4.10** The predicted results of each factor.

The results showed that the probability of obtaining the highest oil content ratio of bio-oil (%yield) in the 95% confidence interval was 24.08% at the temperature variable level of 700 °C ratios of OPS: AC was 80:20 and the pyrolysis time was 40 minutes. When repeating the experiment confirm the predicted result by repeating 5 times at the experimental conditions above. The results showed that the percent yield of crude bio-oil was 24.00%, 21.60%, 22.20%, 21.80%, and 22.00%, with an average of 21.90% ± 0.26, 2.18% deviation from the predicted target.

### 4.4.1 The results of analysis of liquid products (Bio-oil) obtained from the microwave pyrolysis process.

The experiment was to find the optimum conditions for bio-oil production from the developed system. When the bio-oil that has undergone the microwave pyrolysis process has been cooled to room temperature. It was found that the bio-oil was separated into two phases which can be observed with the naked eye, the aqueous phase, which is dark brown. There is a large amount and the top phase and the oil phase (oil phase) are the dark brown-black phase. It is smaller in volume compared to the aqueous phase and is located at the bottom of the container as shown in Figure 4.11.
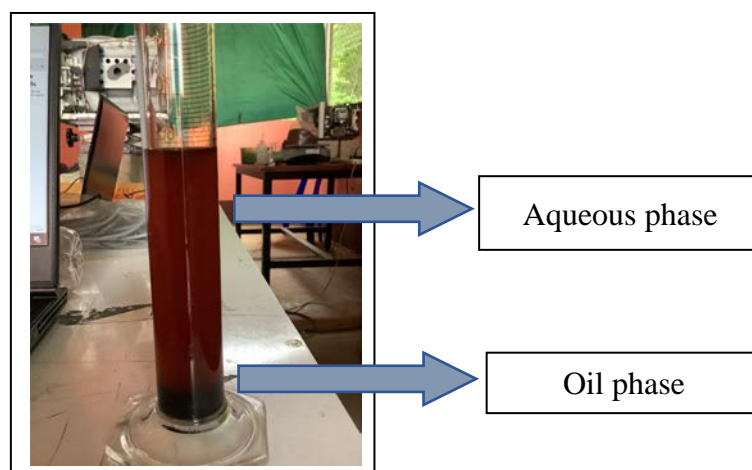


**Figure 4.11** Crude bio-oil obtained by microwave pyrolysis. where the upper part is the aqueous phase. and the lower part is the oil phase.

### 4.4.2 The results of analysis of bio-oil obtained from microwave pyrolysis to test the chemical composition with the Gas Chromatograph-Mass Spectrometer (GC-MS).

The crude bio-oil produced by microwave pyrolysis was collected under various conditions to test the chemical composition with the Gas Chromatograph-Mass Spectrometer (GC-MS). The different experimental conditions were temperature ($^o$C), ratio (OPS: AC) and pyrolysis time for the first condition was the temperature of 700 °C, ratio OPS: AC 80:20, and pyrolysis time of 40 minutes. The second condition was temperature 400 °C, the ratio of OPS: AC 80:20, and pyrolysis time 40 min, and the

third condition was temperature 550°C, ratio of OPS: AC 75:25, and pyrolysis time 35 min, respectively. The results of the chemical composition analysis of samples were obtained from all three conditions. The GC-MS analysis can be shown in Figure 4.12 Table 4.5, Figure 4.13 Table 4.6, and Figure 4.14 Table 4.7 respectively.
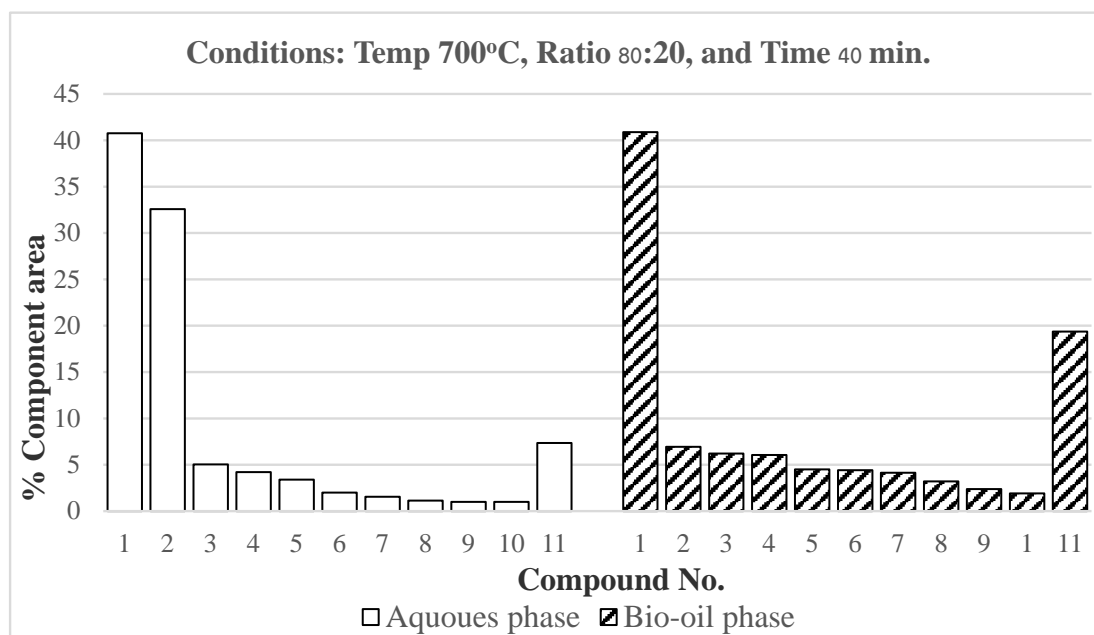


**Figure 4.12** Chemical composition of crude bio-oil in the water phase and oil phase at condition temperature 700 °C, the ratio of oil palm shell to activated carbon 80:20, and time of pyrolysis 40 minutes.

**Table 4.5** Chemical composition of crude bio-oil from GC-MS analysis at condition temperature 700 °C, the ratio of oil palm shell to activated carbon 80:20, and time of pyrolysis 40 minutes.

| No. | Compound Name Aqueous phase | %Component Area | Compound Name Bio-oil phase | %Peak Area |
|---|---|---|---|---|
| 1 | Phenol | 40.76 | Phenol | 40.88 |
| 2 | Acetic acid | 32.57 | Acetic acid | 6.93 |
| 3 | Furfural | 5.03 | Phenol, 2-methoxy- | 6.21 |
| 4 | Phenol, 2-methoxy- | 4.21 | Phenol, 2,6-dimethoxy- | 6.05 |
| 5 | Phenol, 2,6-dimethoxy- | 3.40 | Creosol | 4.51 |
| 6 | 2-Propanone, 1-hydroxy- | 1.99 | Phenol, 4-ethyl-2-methoxy- | 4.42 |
| 7 | Creosol | 1.55 | Furfural | 4.14 |
| 8 | 1-(acetyloxy)-2-propanone | 1.14 | 3,5-Dimethoxy-4-hydroxytoluene | 3.21 |
| 9 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 1.00 | Benzene, 1,2,3-trimethoxy-5-methyl- | 2.38 |
| 10 | 2-Furanmethanol | 1.00 | Phenol, 2-methoxy-4-(1-propenyl)- | 1.91 |
| 11 | Other | 7.35 | Other | 19.36 |
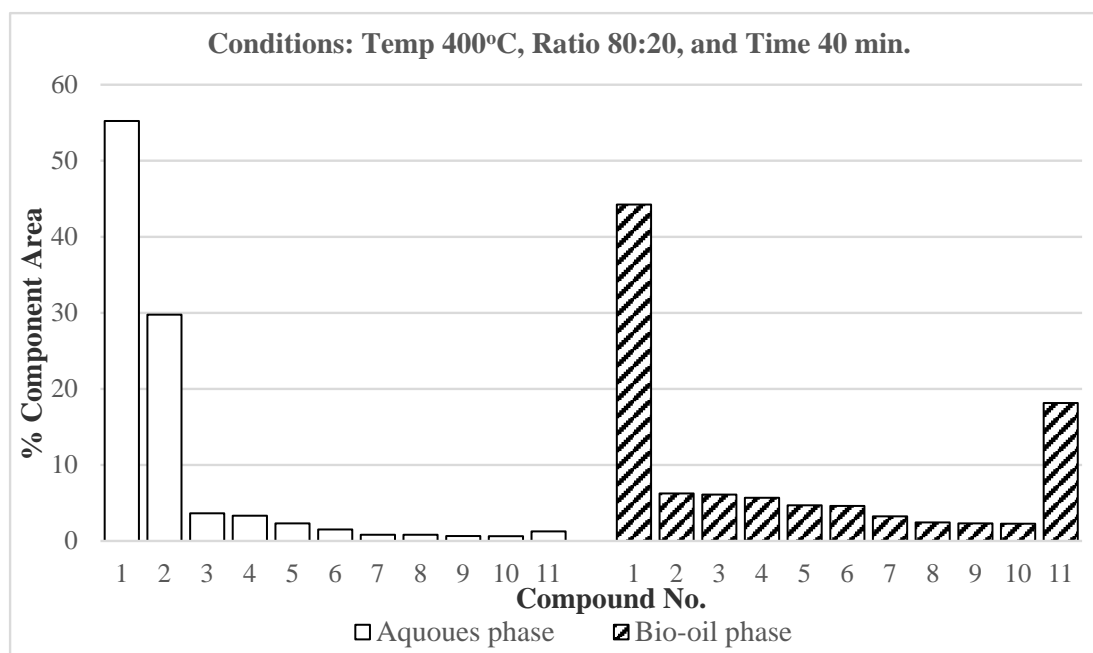
**Figure 4.13** Chemical composition of crude bio-oil in the water phase and oil phase at condition temperature 400 °C, the ratio of oil palm shell to activated carbon 80:20, and time of pyrolysis 40 minutes.

**Table 4.6** Chemical composition of bio-oil phase from GC-MS analysis at condition temperature 400 °C, the ratio of oil palm shell to activated carbon 80:20, and time of pyrolysis 40 minutes.

| No. | Compound Name Aqueous phase | %Component Area | Compound Name Bio-oil phase | %Peak Area |
|-----|------------------------------|------------------|------------------------------|-------------|
| 1 | Acetic acid | 55.22 | Phenol | 44.24 |
| 2 | Phenol | 29.76 | Phenol, 2-methoxy- | 6.25 |
| 3 | Furfural | 3.65 | Acetic acid | 6.10 |
| 4 | 2-Propanone, 1-hydroxy- | 3.32 | Phenol, 2,6-dimethoxy- | 5.69 |
| 5 | Phenol, 2-methoxy- | 2.32 | Phenol, 4-ethyl-2-methoxy- | 4.69 |
| 6 | Phenol, 2,6-dimethoxy- | 1.52 | Furfural | 4.61 |
| 7 | Propanoic acid | 0.83 | 3,5-Dimethoxy-4-hydroxytoluene | 3.25 |
| 8 | 1-(acetyloxy)-2-propanone | 0.82 | Phenol, 2-methoxy-4-(1-propenyl)- | 2.45 |
| 9 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 0.65 | €2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol | 2.31 |
| 10 | 4-Methoxy-2-methyl phenol | 0.64 | Benzene, 1,2,3-trimethoxy-5-methyl- | 2.27 |
| 11 | Other | 1.27 | Other | 18.14 |
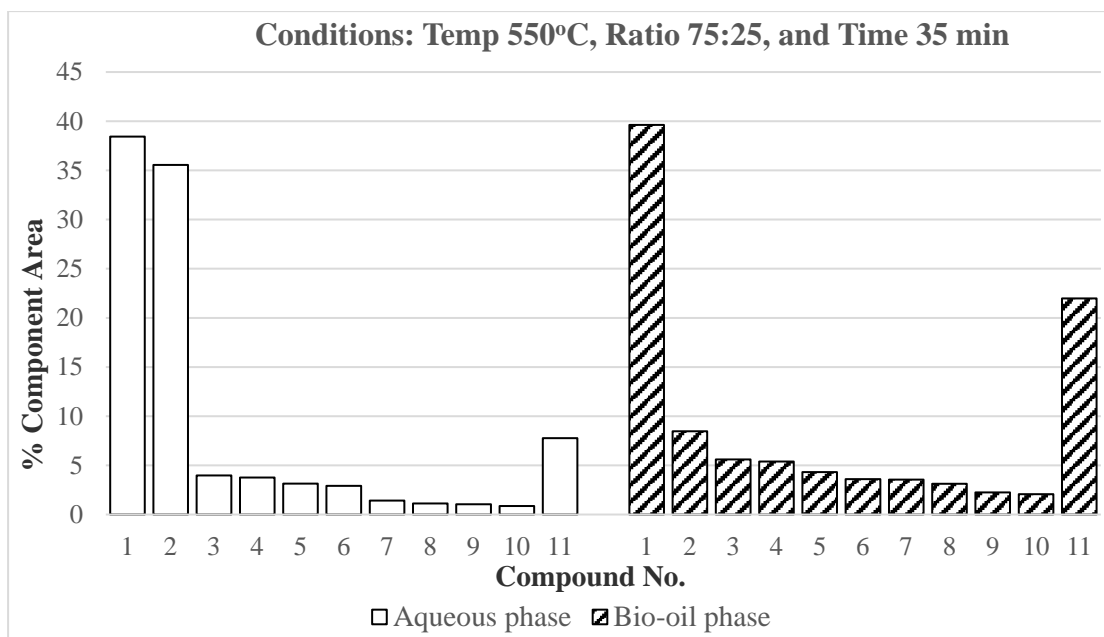
**Figure 4.14** Chemical composition of crude bio-oil in the water phase and oil phase at condition temperature 550 °C, the ratio of oil palm shell to activated carbon 75:25, and time of pyrolysis 35 minutes.

**Table 4.7** Chemical composition of crude bio-oil phase from GC-MS analysis at condition temperature 550 °C, the ratio of oil palm shell to activated carbon 75:25, and time of pyrolysis 35 minutes.

| No. | Compound Name Aqueous phase | %Component Area | Compound Name Bio-oil phase | %Peak Area |
|---|---|---|---|---|
| 1 | Phenol | 38.43 | Phenol | 39.63 |
| 2 | Acetic acid | 35.55 | Acetic acid | 8.47 |
| 3 | Furfural | 3.98 | Phenol, 2-methoxy- | 5.60 |
| 4 | Phenol, 2-methoxy- | 3.76 | Phenol, 2,6-dimethoxy- | 5.40 |
| 5 | 2-Propanone, 1-hydroxy- | 3.14 | Creosol | 4.32 |
| 6 | Phenol, 2,6-dimethoxy- | 2.92 | Phenol, 4-ethyl-2-methoxy- | 3.60 |
| 7 | 2-methoxy-4-methyl-phenol | 1.42 | Furfural | 3.55 |
| 8 | 1-(acetyloxy)-2-propanone | 1.13 | 3,5-Dimethoxy-4-hydroxytoluene | 3.13 |
| 9 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | 1.04 | (E)-2,6-Dimethoxy-4-(prop-1-en-1-yl) phenol | 2.25 |
| 10 | Propanoic acid | 0.87 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | 2.07 |
| 11 | Other | 7.76 | Other | 21.98 |

Chemical composition analysis with GC-MS. It was found that the main chemical compositions of crude bio-oil in the aqueous phase were acetic acid and phenol temperature at 400 °C, and high acetic acid content was found. were 55.22% and 29.76% phenol, as shown in Figure 4.13 and Table 4.6 When the pyrolysis temperature was increased to 550 and 700 °C, the resulting phenol content was higher than that of phenol. acetic acid along with other chemical elements found more clearly It has been shown that increasing the temperature results in the dissociation of acetic acid into many other chemical constituents, as was found in the research (Chuayjumnong, Karrila, Jumrat, & Pianroj, 2020). That when the pyrolysis temperature is higher, the chemical composition of various substances is found as shown in Figure 4.12, Table 4.5, and Figure 4.14, Table 4.7 respectively, and when comparing the phenol content in the bio-oil in both phases (oil and liquid) are approximately the same with phenol content in the range of 29.76 - 44.24%.

**4.4.3 The results analysis of solid products obtained from the microwave pyrolysis process**

**4.4.3.1 The result analysis of proximate and thermal properties of bio-char**

After microwave pyrolysis process the solid product from microwave pyrolysis at production conditions that maximize crude bio-oil content is the temperature of 700 °C, the ratio of palm shell to activated carbon is 80:20 and the pyrolysis time is 40 minutes. It has been sent to the Office of Scientific Instrument and Testing Prince of Songkla University Hatyai campus to analyze properties by proximate analysis by Macro TGA 701, Macro CHNS, CHNS628, LECO, USA, and thermal properties by Bomb Calorimeter, C5000 IKA, Germany. The results are shown in Table 4.8

**Table 4.8** The Proximate analysis and thermal properties of biochar from the microwave pyrolysis process

| Parameter | Result ± SD | | Unit | Method |
|---|---|---|---|---|
| | Oil palm shell | Bio-char from the microwave pyrolysis process | | |
| Moisture | 11.39[1] | 4.88 ± 0.02 % | %wt | ASTM D7582 |
| Volatile | 65.76[1] | 19.62 ± 0.24 % | %wt | ASTM D7582 |
| Fixed carbon | 19.73[1] | 71.84 ± 0.23 % | %wt | ASTM D7582 |
| Ash | 3.12[1] | 3.66 ± 0.01 % | %wt | ASTM D7582 |
| High heating value; H.H.V. | 4,085.16[2] | 7,006 ± 12 % | kcal/kg | BSEN14918 |
| Net heating value | 5,641.53[3] | 6,844 ± 12 % | kcal/kg | BSEN14918 |

**Note ;** [1] (Pianroj, Jumrat, Werapun, Karrila, & Tongurai, 2016), [2] (Qarizada, Mohammadian, Alias, Rahimi, & Yusuf, 2018), and [3](Paul, John, Ndubuisi, Peter, & Godspower, 2015).

In the experiment, it was found that the material is an oil palm shell. which undergoes the microwave pyrolysis process (bio-char) under the condition temperature of 700 °C, the ratio of oil palm shell mixture to the activated carbon is 80:20 and the pyrolysis time is 40 minutes. It has better properties by proximate analysis and thermal properties compared to oil palm shells that have not undergone microwave pyrolysis. It was found that moisture and volatile content were reduced, but the fixed carbon increased, resulting in a higher heating value. This indicates that the microwave pyrolysis processes give biomass material (oil palm shell) better thermal properties, as shown in Table 4.15.

**4.4.3.2 The result analysis of physical properties surface area Average pore diameter and pore volume**

The physical properties analysis of bio-char on surface area Average pore diameter and pore volume Surface area and porosity analyzer (Brunauer-Emmett-Teller; BET), ASAP2460, Micro metrics, USA using Static volumetric $N_2$ gas

adsorption method with degas temperature of sample cleaning 80 ºC. Testing the raw materials (Oil palm shell), the solid product from microwave pyrolysis(bio-char), and activated carbon commercial grade to study and compare Surface physical properties Average pore diameter, and pore volume The data can be shown in Table 4.9 and analyzing the morphology of oil palm shell raw materials and bio-char scanning electron microscope (SEM) at 200x 1000x 2500x 10,000x magnification was used to image the morphology of the two materials after and before microwave pyrolysis process. It is shown in Figure 4.8 and Figure 4.9, respectively.

**Table 4.9** Comparison of properties of palm shell, bio-char, and activated carbon commercial grade

| Parameter | Units | Result | | |
|---|---|---|---|---|
| | | Oil palm shell | Bio-char from the microwave pyrolysis process | *Activated carbon commercial grade |
| BET surface area | m²/g | 0.3600 | 0.5785 | 686.1318 |
| Adsorption average pore diameter | A-degrees | 101.2308 | 275.6726 | 16.6230 |
| Pore volume | cm³/g | 0.000911 | 0.003987 | 0.285139 |

*From a study analyzed by (Chuayjumnong et al., 2020).

a)

b)

c)

d)
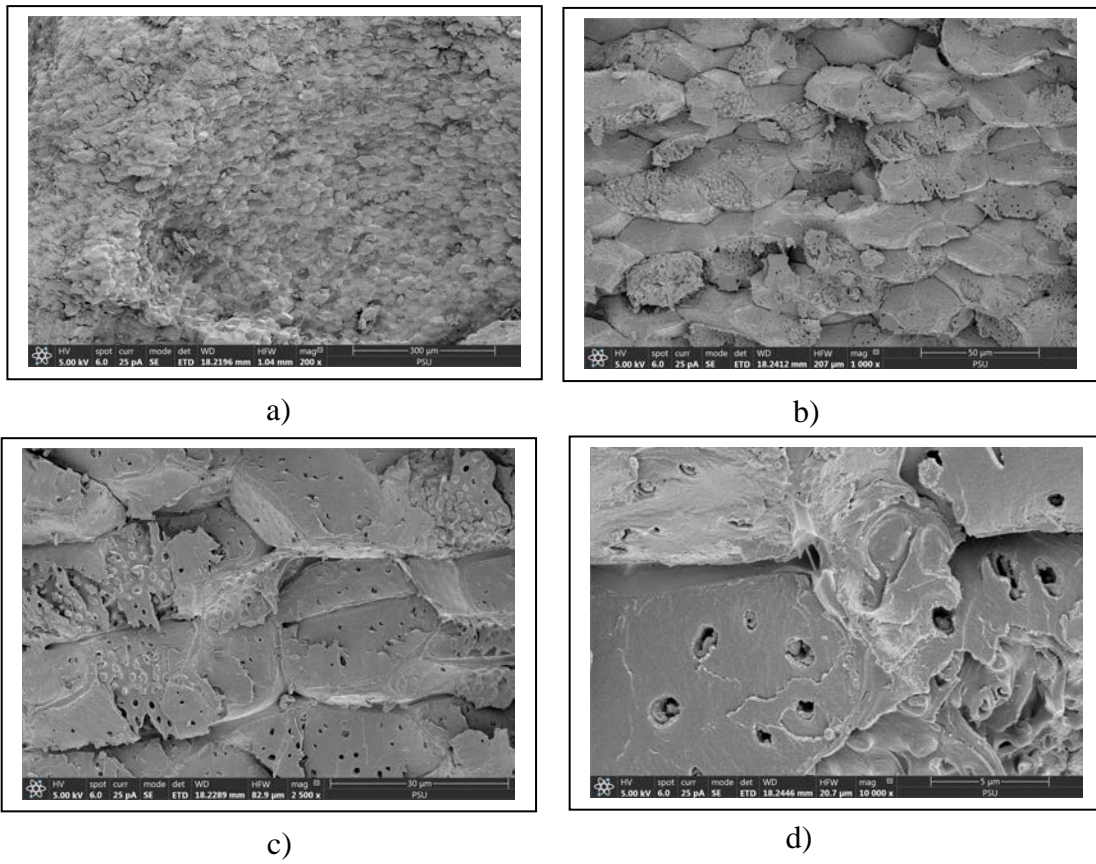
**Figure. 4.15** SEM morphology of OPS at magnifications under scanning electron microscopy at magnification a) 200x b) 1000x c) 2,500x d) 10,000x.
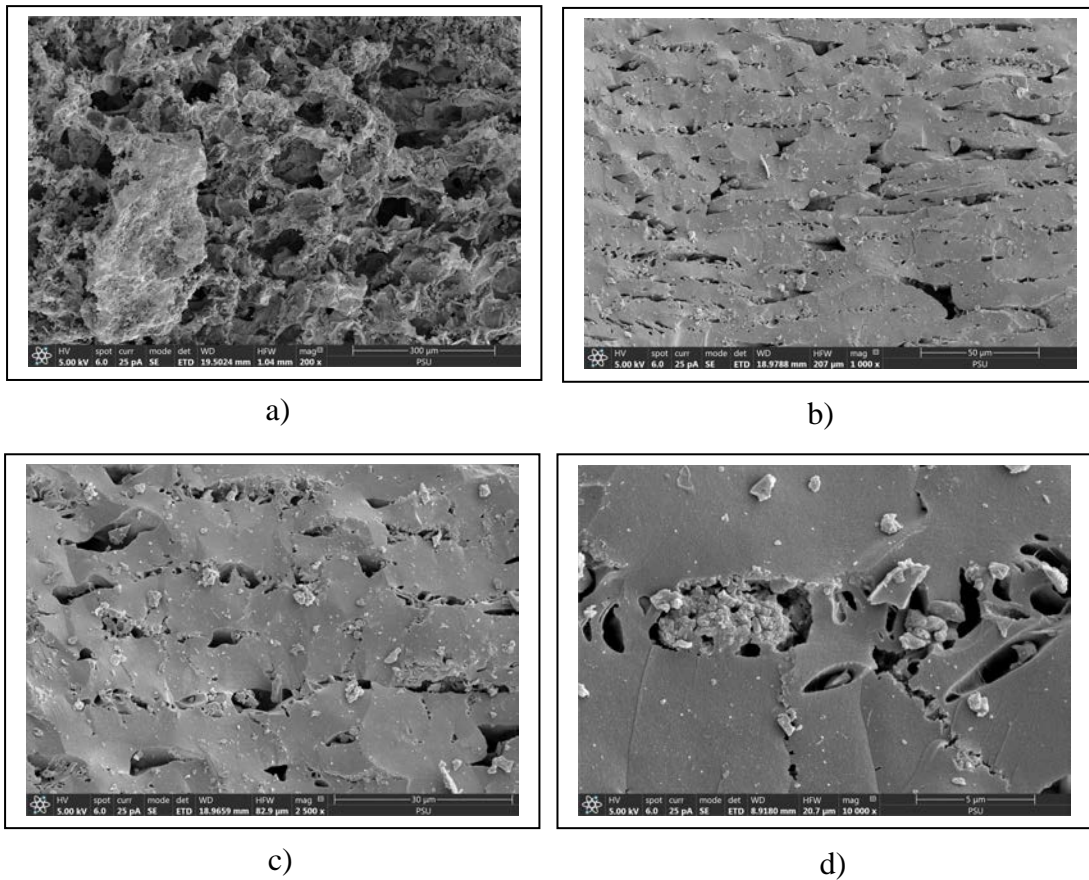
**Figure 4.16** SEM morphology of bio-char at magnifications under scanning electron microscopy at magnification a) 200x b) 1000x c) 2,500x d) 10,000x.

The results showed that the product was in solid phases through the microwave pyrolysis process (bio-char) will have surface area average pore diameter and pore volume increased due to the temperature of pyrolysis is 700°C. in anaerobic conditions, the volatile substance becomes volatile from the raw material (oil palm shell) structure as shown in Figure 4.15. This causes the pore diameter to be larger from 101.2308 A° to 275.6726 A° as shown in Figure 4.15 compared to 4.16. increasing surface area and pore volume as shown in Figure 4.16, but, when comparing bio-char with activated carbon commercial grade the surface content was found to be much less than activated carbon commercial grade. Especially BET surface area and pore volume. Therefore, if using bio-char as activated carbon further chemical or thermal processing is to make the properties of solid products from the microwave pyrolysis process similar to or higher than activated carbon commercial grade.

**4.5 The result of experimental extraction of bio-phenol from crude bio-oil by supercritical fluid extraction with carbon dioxide process**

**4.5.1 The result of extraction of bio-phenol from crude bio-oil by supercritical fluid extraction with carbon dioxide process (scCO₂)**

The results of extraction of crude bio-oil obtained from microwave pyrolysis process by supercritical fluid extraction with carbon dioxide at the condition the ratio of oil palm shell to activated carbon 80:20, the temperature of 700 °C, the pyrolysis time was 40 minutes. which mixes the dispersion enhancer (Spe-ed Matrix) with crude bio-oil. The ratio of bio-oil to Spe-ed Matrix equal to 2:1 (total volume 10 grams) packed into the vessel and loaded in the supercritical fluid extraction with carbon dioxide extractor, respectively. The experiment was carried out according to the conditions specified in Table 3.4 and the $CO_2$ flow rate was constant at 3 liters/minute It was found that the percentage yield of scCO₂ oil (%yield of scCO2 oil) after the extraction time of 30 minutes, it can be shown in Table 4.10.

**Table 4.10** The percentage yield of scCO₂ oil extracted in each experimental conditions.

| No. | Conditions | | | Weigh of Matrix (g) | Weigh of crude bio-oil (g) | Weigh of oil from supercritical with carbon dioxide (g) | %Yield of scCO₂ oil | The average percentage yield of scCO₂ oil |
|---|---|---|---|---|---|---|---|---|
| | Temp (ºC) | Pressure (bar) | Time (min.) | | | | | |
| 1 | 50 | 300 | 30 | 10.00 | 20.00 | 12.6537 | 48.80 | 50.04 |
| 2 | 50 | 300 | 30 | 10.00 | 20.00 | 10.2621 | 51.28 | |
| 3 | 50 | 400 | 30 | 10.00 | 20.00 | 12.9786 | 43.18 | 45.74 |
| 4 | 50 | 400 | 30 | 10.00 | 20.00 | 9.6646 | 48.29 | |
| 5 | 60 | 350 | 30 | 10.00 | 20.00 | 12.3424 | 61.69 | 56.04 |
| 6 | 60 | 350 | 30 | 10.00 | 20.00 | 10.1013 | 50.38 | |
| 7 | 70 | 300 | 30 | 10.00 | 20.00 | 13.5698 | 33.34 | 41.50 |
| 8 | 70 | 300 | 30 | 10.00 | 20.00 | 9.9482 | 49.65 | |
| 9 | 70 | 400 | 30 | 10.00 | 20.00 | 13.4589 | 49.97 | 52.21 |
| 10 | 70 | 400 | 30 | 10.00 | 20.00 | 10.9664 | 54.44 | |

The physical characteristics of oils are obtained by supercritical fluid extraction methods ($scCO_2$ oil) can be seen as light brown and has less viscosity compared to crude bio-oil with dark brown color and high viscosity. The characteristics of crude bio-oil and $scCO_2$ oil under different conditions can be shown in Figure 4.17 which shows the different appearances between crude bio-oil and $scCO_2$ oils under various.
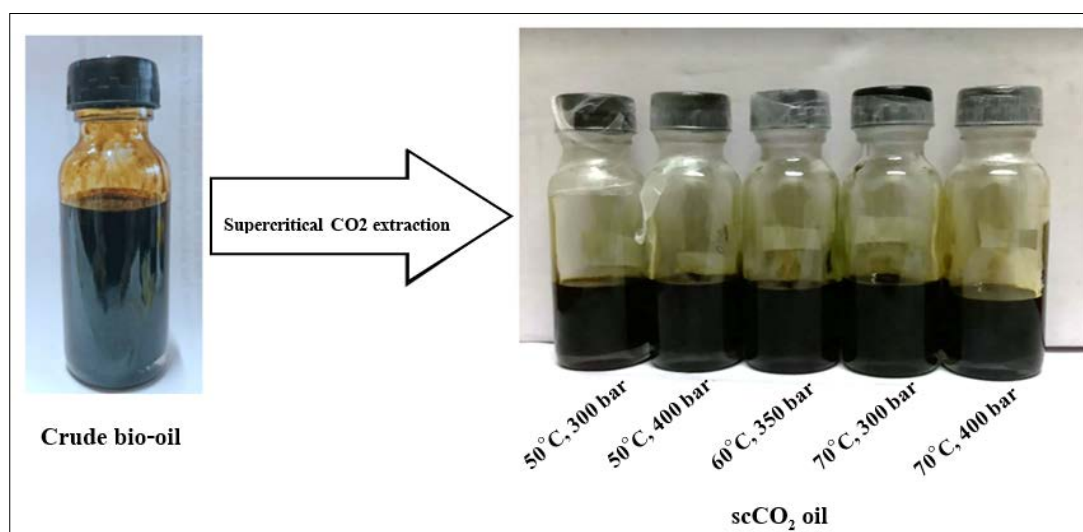


**Figure 4.17** Comparison of appearance between crude bio-oil and $scCO_2$ oil obtained from experiments under various conditions.

The supercritical oil ($scCO_2$ oil) was obtained from bio-oil extraction with carbon dioxide in each experimental condition. The chemical composition was analyzed by GC-MS. The percentage of $scCO_2$ oil (%yield of $scCO_2$ oil) obtained from this study showed that under the experimental conditions, the extraction temperature was 70 °C and the extraction pressure was 300 bar. The extraction time was 30 minutes, the flow rate of carbon dioxide was 3.0 liters/minute, and the Spe-ed Matrix was used as a dispersing agent. The highest percentage of $scCO_2$ oil was 67.81%. When compared with previous research, it was found that research studied (Feng & Meier, 2017) The highest percentage of scCO2 oil was 13 -14% at the extraction temperature of 60 °C, the extraction pressure was 300 bar, the extraction time was 4 hours, the carbon dioxide flow rate was 3.5 liters/min, and silicon dioxide was used. ($SiO_2$) as a dispersant from this research, it was found that the percentage of $scCO_2$ oil depends on

various factors. where pressure and temperature affect the density of the solvent, when considering the effect of pressure. It was found that high extraction pressure results in high solvent densities and consequently a high percentage of $scCO_2$ oil, when the temperature was higher the density of the solvent was decreased (Foster et al., 1991) That is, the mass transfer rate increased, resulting in high extraction efficiency. up to including intermolecular force between the pore surface of the dispersing substance to the crude bio-oil which is the result of mass transfer and selective extraction. The selectivity results in the percentage content of scCO2 oil and the chemical composition of extracted $scCO_2$ oil will vary according to the above factors.

**4.5.2 The results of oil properties analysis from the supercritical fluid extraction with the carbon dioxide process**

The $scCO_2$ oil was obtained from supercritical fluid extraction with carbon dioxide. The $scCO_2$ oil in each of the experimental conditions in Table 4.17 was sent for chemical composition determination in $scCO_2$ oil by the Gas Chromatography-Mass Spectrometer (GC-MS, GC 7890B, MSD 5977A, Agilent, USA) Office of Scientific Instrument and Testing Prince of Songkla University Hatyai Campus. Comparing the results of the chemical composition that can be checked at different time intervals compared with crude bio-oil before $scCO_2$ processing, the effect of chemical composition can be seen in Figure 4.18.
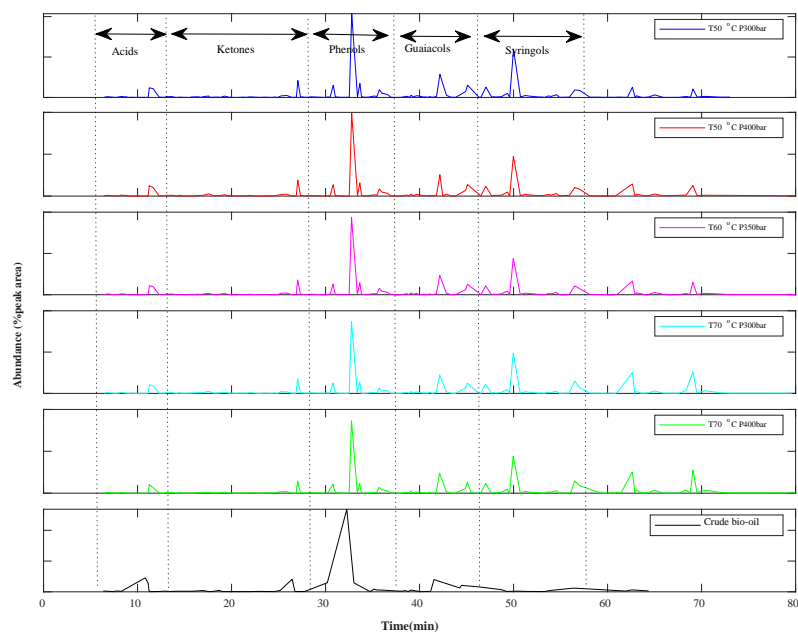
**Figure 4.18** Chemical composition of bio-oil from scCO₂ process with GC-MS analyzer

In the analysis results of Figure 4.18, it was found that the chemical composition curves of scCO₂ oil under all experimental conditions had a large percentage of the area under the curve (%peak area of Abundance) broken up into a large number of curves over the time during the investigation. 30-70 minutes. It has been found that several chemical compositions are different from crude bio-oil. Because crude bio-oil is a bio-oil obtained by microwave pyrolysis of oil palm shells in which palm shells are the main raw material of lignin (Hossain, Jewaratnam, & Ganesan, 2016) Through thermal dissociation or pyrolysis, the main product is phenol and aromatic compounds, up to about 80% peak area, and the main compound found in phenol up to about 40% peak area after scCO₂ process, This extraction is an extraction that is highly specific to each extract. resulting in different extracts compared to crude bio-oil. This can be seen from the %peak area that differs over the analysis interval when comparing scCO₂ oil and crude bio-oil. his is shown in Figure 4.18, as is found in the research of (Chan, Yusup, Quitain, Uemura, & Loh, 2017) and (Feng & Meier, 2015).

The chemical composition analysis of crude bio-oil and scCO₂ oil was categorized into 10 chemical groups: acid, ester, aldehyde, ketone, furan, pyran, phenol,

guaiacol, syringol, and others. It was found that the $scCO_2$ process is an extraction process with different extraction properties depending on the solvent. In this research, supercritical carbon dioxide is used to extract chemical constituents in acids, esters, and others. to have the enrichment after the $scCO_2$ process (Feng & Meier, 2016) as shown in Figure 4.19 and Table 4.17 which acid type with a high %peak area after the $scCO_2$ process was dodecanoic acid. The percentage peak area of $scCO_2$ oil for all experimental conditions was 11.684±0.971. the n-Hexadecnoic acid mean %peak area of $scCO_2$ oil for all experimental conditions was 2.885±0.666 and the mean %peak area. The $scCO_2$ oil for all experimental conditions was octadecanoic acid, 4.538±1.508, respectively. The three predominant products after $scCO_2$ treatment were observed as in previous work (Chan et al., 2017) and (Naik, Goud, Rout, & Dalai, 2010) In addition, from the GC-MS analyzer data, it was found that some acids were not detectable in crude bio-oil due to their very small proportion when in the form of crude bio-oil but when processed by $scCO_2$. The concentration was then increased to be measured with a GC-MS analyzer for $scCO_2$ oil, which was also found in previous studies (Chan et al., 2017). The chemistry of crude bio-oil and $scCO_2$ oil for all experimental conditions with the GC-MS analyzer, it can be shown as shown in Figure 4.19.
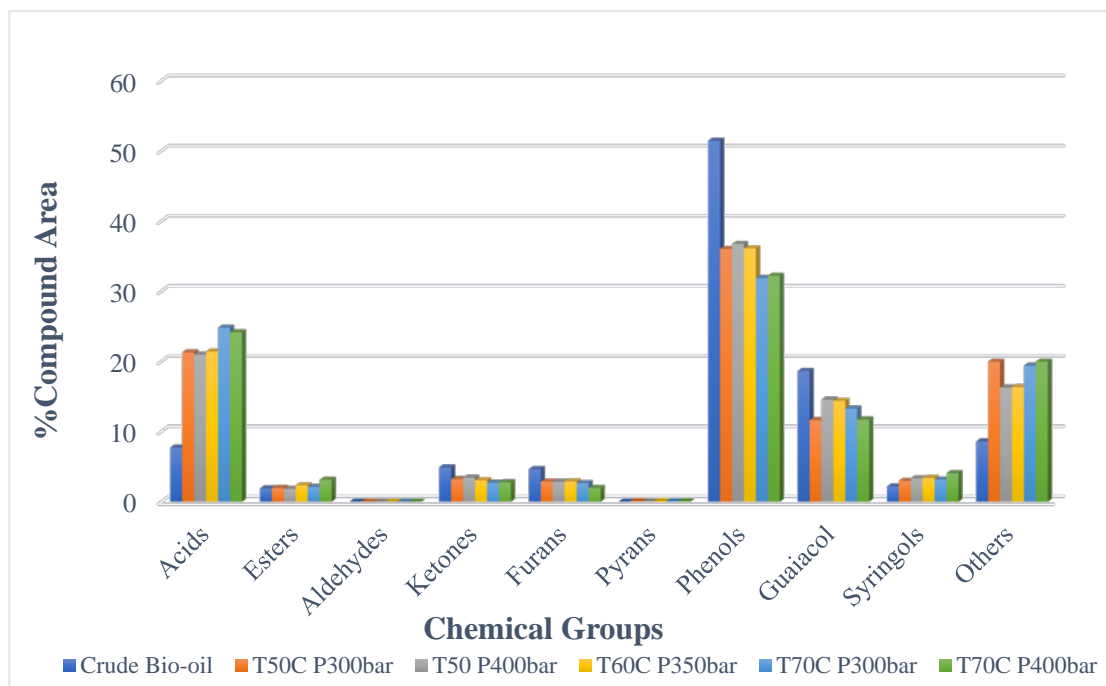
**Figure 4.19** Chemical groups found from crude bio-oil and scCO$_2$ oil for each condition.

**Table 4.11** Percentage area (%peak area) of chemical constituents found in crude biomass and scCO$_2$ for each condition analyzed by GC-MS.

| Chemical Groups | % of crude bio-oil | Percentage of scCO$_2$ Oil | | | | |
|---|---|---|---|---|---|---|
| | | T 50°C, P 300 bar | T 50°C, P 400 bar | T 60°C, P 350 bar | T 70°C, P 300 bar | T 70°C, P 400 bar |
| Acids | 7.717 | 21.274 | 20.973 | 21.408 | 24.800 | 24.146 |
| Esters | 1.893 | 1.966 | 1.828 | 2.337 | 2.111 | 3.116 |
| Aldehydes | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ketones | 4.893 | 3.208 | 3.415 | 3.057 | 2.687 | 2.768 |
| Furans | 4.637 | 2.877 | 2.843 | 2.898 | 2.636 | 1.961 |
| Pyrans | 0.000 | 0.094 | 0.073 | 0.076 | 0.070 | 0.079 |
| Phenols | 51.461 | 36.028 | 36.722 | 36.115 | 31.879 | 32.199 |
| Guaiacol | 18.629 | 11.624 | 14.547 | 14.386 | 13.276 | 11.712 |
| Syringes | 2.173 | 2.972 | 3.340 | 3.380 | 3.152 | 4.053 |
| Others | 8.596 | 19.957 | 16.261 | 16.342 | 19.388 | 19.966 |

**Table 4.12** Chemical composition of crude bio-oil and scCO₂ oil for all conditions analyzed by GC-MS.

| No. | Compound | Formula | CAS No. | | N004 | N009 | N016 | N023 | N030 |
|---|---|---|---|---|---|---|---|---|---|
| | Acids: | | | 7.717 | 21.274 | 20.973 | 21.408 | 24.800 | 24.146 |
| 1 | Acetic acid | $C_2H_4O_2$ | 64-19-7 | 6.931 | 2.657 | 2.977 | 2.758 | 2.481 | 2.510 |
| 2 | Propanoic acid | $C_3H_6O_2$ | 79-09-4 | 0.278 | 0.076 | 0.192 | 0.123 | 0.076 | 0.085 |
| 3 | Butanoic acid | $C_4H_8O_2$ | 107-92-6 | - | 0.078 | 0.103 | 0.074 | 0.088 | 0.067 |
| 4 | Pentanoic acid | $C_5H_{10}O_2$ | 109-52-4 | 0.129 | - | - | - | - | - |
| 5 | Dodecanoic acid | $C_{12}H_{24}O_2$ | 143-07-7 | - | 13.306 | 11.460 | 11.129 | 11.723 | 10.802 |
| 6 | Tetradecanoic acid | $C_{14}H_{28}O_2$ | 544-63-8 | - | 2.080 | 2.475 | 2.733 | 3.580 | 3.558 |
| 7 | n-Hexadecanoic acid | $C_{16}H_{32}O_2$ | 57-10-3 | 0.379 | 2.816 | 3.481 | 4.191 | 6.020 | 6.181 |
| 8 | Octadecanoic acid | $C_{18}H_{36}O_2$ | 57-11-4 | - | 0.261 | 0.285 | 0.400 | 0.834 | 0.943 |
| | Esters: | | | 1.893 | 1.966 | 1.828 | 2.337 | 2.111 | 3.116 |
| 9 | Propanoic acid, ethenyl ester | $C_5H_8O_2$ | 105-38-4 | - | 0.005 | - | - | - | - |
| 10 | Levulinic acid, methyl ester | $C_6H_{10}O_3$ | 624-45-3 | - | - | 0.019 | - | - | - |
| 11 | Benzoic acid, 4-hydroxy-, methyl ester | $C_8H_8O_3$ | 99-76-3 | 0.947 | 0.446 | 0.513 | 0.586 | 0.556 | 0.945 |
| 12 | Hexadecanoic acid, methyl ester | $C_{17}H_{34}O_2$ | 112-39-0 | - | 0.230 | 0.231 | 0.254 | 0.335 | 0.270 |
| 13 | 9-Octadecenoic acid (Z)-, methyl ester | $C_{19}H_{36}O_2$ | 112-62-9 | - | 0.219 | - | 0.287 | - | 0.251 |
| 14 | Benzoic acid, 4-(acetyloxy)-3-methoxy-, methyl ester | $C_{11}H_{12}O_5$ | 35400-19-2 | - | - | 0.113 | 0.114 | - | - |
| 15 | Benzoic acid, 3-hydroxy-, methyl ester | $C_8H_8O_3$ | 19438-10-9 | - | 0.050 | - | 0.047 | - | 0.083 |
| 16 | Benzoic acid, 4-hydroxy-3,5-dimethoxy-, methyl ester | $C_{10}H_{12}O_5$ | 884-35-5 | - | 0.012 | - | - | - | - |
| 17 | Acetic acid, hydroxy-, methyl ester | $C_3H_6O_3$ | 96-35-5 | - | 0.016 | 0.016 | 0.016 | 0.009 | 0.008 |
| 18 | 3-Chloropropionic acid, 2-tetrahydro furyl methyl ester | $C_8H_{13}ClO_3$ | 4647-34-1 | - | - | - | - | 0.019 | - |
| 19 | Octanoic acid, methyl ester | $C_9H_{18}O_2$ | 111-11-5 | - | 0.015 | - | - | - | - |
| 20 | Dodecanoic acid, methyl ester | $C_{13}H_{26}O_2$ | 111-82-0 | - | 0.407 | 0.422 | 0.448 | 0.490 | 0.424 |

| No. | Compound | Formula | CAS No. | | N004 | N009 | N016 | N023 | N030 |
|---|---|---|---|---|---|---|---|---|---|
| 21 | Benzoic acid, 4-hydroxy-, methyl ester | $C_8H_8O_3$ | 99-76-3 | 0.947 | 0.446 | 0.513 | 0.586 | 0.556 | 0.945 |
| 22 | Bis(2-Ethylhexyl) phthalate | $C_{24}H_{38}O_4$ | 117-81-7 | - | 0.122 | - | - | 0.148 | 0.189 |
| | Aldehydes: | | | - | - | - | - | - | - |
| 23 | Propionaldehyde, 3-hydroxy | | 2134-29-4 | - | - | - | - | - | - |
| 24 | Butanedial / Propanal | | 638-37-9 | - | - | - | - | - | - |
| 25 | Acetaldehyde, hydroxy- | | 141-46-8 | - | - | - | - | - | - |
| 26 | Butandisl | | 638-37-9 | - | - | - | - | - | - |
| 27 | Benzaldehyde, 2-hydroxy(Salicylalclehyd) | | 90-02-8 | - | - | - | - | - | - |
| 28 | Benzaldehyde, 2-hydroxy-5-methoxy- | | 672-13-9 | - | - | - | - | - | - |
| 29 | Benzaldehyde, 3-hydroxy-4-methyl- | | 57295-30-4 | - | - | - | - | - | - |
| | Ketones: | | | 4.893 | 3.208 | 3.415 | 3.057 | 2.687 | 2.768 |
| 30 | 2-Propanone, 1-hydroxy- | $C_3H_6O_2$ | 116-09-6 | 0.395 | 0.211 | 0.217 | 0.244 | 0.217 | 0.222 |
| 31 | 2-Butanone | $C_4H_8O$ | 78-93-3 | 0.079 | - | - | - | - | - |
| 32 | 1-Hydroxy-2-butanone | $C_4H_8O_2$ | 5077-67-8 | 0.194 | 0.224 | 0.261 | 0.186 | 0.105 | 0.068 |
| 33 | 2-Propanone, 1-(acetyloxy)- | $C_5H_8O_3$ | 592-20-1 | 0.573 | - | - | - | - | - |
| 34 | 2-Cyclopenten-1-one | $C_5H_6O$ | 930-30-3 | 0.395 | 0.292 | 0.295 | 0.282 | 0.262 | 0.200 |
| 35 | 2-Cyclopenten-1-one, 2,3-dimethyl- | $C_7H_{10}O$ | 1121-05-7 | - | 0.106 | 0.212 | 0.098 | 0.144 | 0.190 |
| 36 | 2-Cyclopenten-1-one, 2-methyl- | $C_6H_8O$ | 1120-73-6 | 0.326 | 0.128 | 0.143 | 0.162 | 0.104 | 0.108 |
| 37 | 2-Cyclopenten-1-one, 3-methyl- | $C_6H_8O$ | 2758-18-1 | 0.335 | 0.253 | 0.251 | 0.242 | 0.214 | 0.205 |
| 38 | 2-Cyclopenten-1-one, 2-hydroxy- | $C_5H_6O_2$ | 10493-98-8 | 0.216 | - | - | - | - | - |
| 39 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | $C_6H_8O_2$ | 80-71-7 | 0.690 | 0.553 | 0.549 | 0.531 | 0.461 | 0.485 |
| 40 | 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- | $C_7H_{10}O_2$ | 21835-01-8 | 0.125 | 0.169 | 0.165 | 0.154 | 0.142 | 0.134 |
| 34 | 2-Cyclopenten-1-one | $C_5H_6O$ | 930-30-3 | 0.395 | 0.292 | 0.295 | 0.282 | 0.262 | 0.200 |
| 35 | 2-Cyclopenten-1-one, 2,3-dimethyl- | $C_7H_{10}O$ | 1121-05-7 | - | 0.106 | 0.212 | 0.098 | 0.144 | 0.190 |
| 36 | 2-Cyclopenten-1-one, 2-methyl- | $C_6H_8O$ | 1120-73-6 | 0.326 | 0.128 | 0.143 | 0.162 | 0.104 | 0.108 |
| 37 | 2-Cyclopenten-1-one, 3-methyl- | $C_6H_8O$ | 2758-18-1 | 0.335 | 0.253 | 0.251 | 0.242 | 0.214 | 0.205 |
| 38 | 2-Cyclopenten-1-one, 2-hydroxy- | $C_5H_6O_2$ | 10493-98-8 | 0.216 | - | - | - | - | - |

| No. | Compound | Formula | CAS No. | | N004 | N009 | N016 | N023 | N030 |
|-----|----------|---------|---------|---|------|------|------|------|------|
| 39 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- | $C_6H_8O_2$ | 80-71-7 | 0.690 | 0.553 | 0.549 | 0.531 | 0.461 | 0.485 |
| 40 | 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- | $C_7H_{10}O_2$ | 21835-01-8 | 0.125 | 0.169 | 0.165 | 0.154 | 0.142 | 0.134 |
| 41 | 2-Cyclohexen-1-one | $C_6H_8O$ | 930-68-7 | - | - | - | - | - | 0.018 |
| 42 | 1-Hydroxy-2-butanone | $C_4H_8O_2$ | 5077-67-8 | 0.194 | 0.224 | 0.261 | 0.186 | 0.105 | 0.068 |
| 43 | 1,2-Cyclopentanedione | $C_5H_6O_2$ | 3008-40-0 | - | 0.089 | 0.114 | 0.105 | 0.093 | 0.091 |
| 44 | 2-Butanone, 1-(acetyloxy)- | $C_6H_{10}O_3$ | 1575-57-1 | 0.177 | 0.011 | 0.020 | - | 0.018 | 0.042 |
| 45 | 2-Cyclopenten-1-one, 2,3,4-trimethyl- | $C_8H_{12}O$ | 28790-86-5 | 0.000 | 0.026 | 0.029 | 0.025 | 0.030 | 0.022 |
| 46 | 2-Cyclopenten-1-one, 2-hydroxy- | $C_5H_6O_2$ | 10493-98-8 | 0.216 | - | - | - | - | - |
| 47 | 2-Butanone, 1-(acetyloxy)- | $C_6H_{10}O_3$ | 1575-57-1 | 0.177 | 0.011 | 0.020 | - | 0.018 | 0.042 |
| 48 | ETHYL CYCLOPENTENOLONE | $C_7H_{10}O_2$ | 21835-01-8 | 0.125 | 0.169 | 0.165 | 0.154 | 0.142 | 0.134 |
| 49 | 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- | $C_{10}H_{12}O_3$ | 2503-46-0 | 0.675 | 0.743 | 0.713 | 0.688 | 0.634 | 0.742 |
| 50 | Acetonylacetone(Hexandione,2.5-) | | 110-13-4 | - | - | - | - | - | - |
| 51 | Acetoin (Hydroxy-2-butanone,3-) | | 513-86-0 | - | - | - | - | - | - |
| 52 | Cylopenten-1-one,3-ethyl-2- | | 5682-69-9 | - | - | - | - | - | - |
| 53 | 3-Pentanone | | 96-22-0 | - | - | - | - | - | - |
| 54 | 2-Butanone,1-hydroxy-3-methyl- | | 36960-22-2 | - | - | - | - | - | - |
| | Furans: | | | 4.637 | 2.877 | 2.843 | 2.898 | 2.636 | 1.961 |
| 56 | 2(5H)-Furanone | $C_4H_4O_2$ | 497-23-4 | - | 0.060 | -0.002 | 0.052 | 0.045 | 0.046 |
| 57 | 3-furan | | 498-60-2 | - | - | - | - | - | - |
| 58 | 2-furan-carboxaldehyde | $C_5H_4O_2$ | 98-01-1 | 4.135 | 2.437 | 2.468 | 2.470 | 2.233 | 1.612 |
| 59 | 2-Furancarboxaldehyde, 5-methyl- | $C_6H_6O_2$ | 620-02-0 | 0.298 | 0.133 | 0.121 | 0.109 | 0.096 | 0.104 |
| 60 | | | 67-14-0 | - | - | - | - | - | - |
| 61 | Ethanone, 1-(2-furanyl)- | $C_6H_6O_2$ | 1192-62-7 | 0.204 | 0.248 | 0.256 | 0.267 | 0.262 | 0.200 |
| 62 | Furan-2-one,5-methyl-,(5H)- | | 591-11-7 | - | - | - | - | - | - |
| 63 | Furan-2-one,3-methyl-,(5H)- | | 22122-36-7 | - | - | - | - | - | - |

| No. | Compound | Formula | CAS No. | | N004 | N009 | N016 | N023 | N030 |
|---|---|---|---|---|---|---|---|---|---|
| 64 | Butyrolactone | | 96-48-0 | - | - | - | - | - | - |
| 65 | 2(5H)-Furanone,5-methyl- | | 591-11-7 | - | - | - | - | - | - |
| 66 | Furan,tetrahydro-2-(methoxymethyl)- | | 19354-27-9 | - | - | - | - | - | - |
| 67 | Furan,-2-one, 4-methyl-(5H)- | | 6124-79-4 | - | - | - | - | - | - |
| 68 | Furan,-2-one, 2,5-dihydro-3,5-dimethyl- | | 5584-69-0 | - | - | - | - | - | - |
| 69 | Furan, tetrahydro-2-methyl- | | 96-47-9 | - | - | - | - | - | - |
| 70 | Butyrolactone, 2-hydroxy | | 19444-84-9 | - | - | - | - | - | - |
| 71 | Tetrahydrofuran (trans), 2,5-dimethoxy- | | 130321-68-5 | - | - | - | - | - | - |
| | Pyrans: | | | - | 0.094 | 0.073 | 0.076 | 0.070 | 0.079 |
| 72 | Maltol | $C_6H_6O_3$ | 118-71-8 | - | 0.094 | 0.073 | 0.076 | 0.070 | 0.079 |
| | Phenols: | | | 51.461 | 36.028 | 36.722 | 36.115 | 31.879 | 32.199 |
| 73 | Phenol | $C_6H_6O$ | 108-95-2 | 40.878 | 23.136 | 23.833 | 23.651 | 20.905 | 21.029 |
| 74 | Cresol,p- (Phenol, 4-methyl-) | $C_7H_8O$ | 106-44-5 | 1.342 | 2.131 | 2.040 | 1.985 | 1.526 | 1.671 |
| 75 | Cresol,o- | | 95-48-7 | - | - | - | - | - | - |
| 76 | Cresol,m- (Phenol, 3-methyl-) | $C_7H_8O$ | 108-39-4 | 0.915 | 1.199 | 1.142 | 1.100 | 0.781 | 1.004 |
| 77 | Phenol, 2,5-dimethyl- | $C_8H_{10}O$ | 95-87-4 | - | 0.095 | - | 0.082 | 0.080 | 0.076 |
| 78 | Phenol, 2,4-dimethyl- | | 105-67-9 | - | - | - | - | - | - |
| 79 | Phenol, 2,6-dimethyl- | $C_8H_{10}O$ | 576-26-1 | - | 0.089 | 0.100 | 0.080 | 0.080 | 0.070 |
| 80 | 2-Methoxy-4-vinyl phenol | $C_9H_{10}O_2$ | 7786-61-0 | 0.853 | 0.496 | 0.502 | 0.460 | 0.416 | 0.358 |
| 81 | Phenol, 2,6-dimethoxy- (Syringol) | $C_8H_{10}O_3$ | 91-10-1 | 6.055 | 6.362 | 6.158 | 5.950 | 5.377 | 5.869 |
| 82 | trans-Isoeugenol | $C_{10}H_{12}O_2$ | 5932-68-3 | 0.208 | 1.622 | 1.620 | 1.534 | 1.465 | 1.361 |
| 83 | 3,5-Dimethoxy-4-hydroxytoluene | $C_9H_{12}O_3$ | 6638-05-7 | - | - | - | - | - | - |

| No. | Compound | Formula | CAS No. | | N004 | N009 | N016 | N023 | N030 |
|-----|----------|---------|---------|------|------|------|------|------|------|
| 84 | Phenol, 2-methoxy-4-propyl- | $C_{10}H_{14}O_2$ | 2785-87-7 | 0.869 | 0.779 | 0.795 | 0.760 | 0.751 | 0.637 |
| 85 | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | $C_{11}H_{14}O_3$ | 6627-88-9 | 0.341 | 0.119 | 0.534 | 0.513 | 0.498 | 0.125 |
| | Guaiacol (methoxy phenols): | | | 18.629 | 11.624 | 14.547 | 14.386 | 13.276 | 11.712 |
| 86 | Phenol, 2-methoxy- | $C_7H_8O_2$ | 90-05-1 | 6.206 | 4.686 | 4.614 | 4.537 | 4.161 | 3.533 |
| 87 | Phenol, 2-methoxy-3-methyl- | $C_8H_{10}O_2$ | 18102-31-3 | - | 0.141 | - | 0.137 | 0.130 | 0.101 |
| 88 | Creosol | $C_8H_{10}O_2$ | 93-51-6 | 4.507 | 3.374 | 3.276 | 3.200 | 2.989 | 2.619 |
| 89 | Phenol, 4-ethyl-2-methoxy- | $C_9H_{12}O_2$ | 2785-89-9 | 4.421 | 0.122 | 3.798 | 3.687 | 3.322 | 2.829 |
| 90 | Eugenol | $C_{10}H_{12}O_2$ | 97-53-0 | 0.295 | 0.315 | - | - | - | - |
| 91 | Phenol, 2-methoxy-4-(1-propenyl)- | $C_{10}H_{12}O_2$ | 97-54-1 | 1.914 | - | - | - | - | - |
| 92 | Phenol, 2-methoxy-4-(1-propenyl)-, (E)- | $C_{10}H_{12}O_2$ | 5932-68-3 | 0.208 | 1.622 | 1.620 | 1.534 | 1.465 | 1.361 |
| 93 | Apocynin | $C_9H_{10}O_3$ | 498-02-2 | 0.168 | 0.065 | 0.070 | 0.058 | 0.060 | 0.055 |
| 94 | 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- | $C_{10}H_{12}O_3$ | 2503-46-0 | 0.675 | 0.743 | 0.713 | 0.688 | 0.634 | 0.742 |
| 95 | 2-Methoxy-5-methyl phenol | $C_8H_{10}O_2$ | 1195-09-1 | - | 0.178 | 0.131 | 0.172 | 0.182 | 0.140 |
| 96 | Vanillin | $C_8H_8O_3$ | 121-33-5 | 0.235 | 0.380 | 0.326 | 0.374 | 0.334 | 0.333 |
| | Syringols: | | | 2.173 | 2.972 | 3.340 | 3.380 | 3.152 | 4.053 |
| 97 | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | $C_{11}H_{14}O_3$ | 6627-88-9 | 0.341 | 0.119 | 0.534 | 0.513 | 0.498 | 0.660 |
| 98 | (E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol | $C_{11}H_{14}O_3$ | 20675-95-0 | 1.832 | 1.924 | 1.954 | 1.858 | 1.670 | 2.201 |
| 99 | Benzaldehyde, 4-hydroxy-3,5-dimethoxy- | $C_9H_{10}O_4$ | 134-96-3 | - | 0.048 | 0.048 | 0.041 | 0.044 | 0.065 |
| 100 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | $C_{10}H_{12}O_4$ | 2478-38-8 | - | 0.145 | 0.142 | 0.148 | 0.151 | 0.210 |
| 101 | 1-Propanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | $C_{11}H_{14}O_4$ | 5650-43-1 | - | 0.032 | 0.073 | 0.120 | 0.073 | 0.044 |
| 102 | Syringylacetone | $C_{11}H_{14}O_4$ | 19037-58-2 | - | 0.704 | 0.589 | 0.701 | 0.717 | 0.873 |

**4.6 The results of the cost analysis of the product**

      **4.6.1 The estimated cost of crude bio-oil**

            In this research study, the estimated cost of both types of products from the microwave pyrolysis process (crude bio-oil) and supercritical fluid extraction with carbon dioxide process ($scCO_2$ oils) can be calculated according to equation (4.3)

$$\text{Product cost (Baht/milliliters)} = (\text{Materials+Electricity})/ \text{ Volume of product} \quad (4.3)$$

Details of costs for estimates of crude bio-oil and $scCO_2$ are shown in Table 4.13.

**Table 4.13** Details of costs in the cost estimation of crude bio-oil and $scCO_2$ oil
              (Price as of 1 October 2021)

| No. | Details | Price | Unit |
|-----|---------|-------|------|
| 1 | Oli palm shell | 2.6 | Baht/kg |
| 2 | Activated carbon commercial grade | 20 | Baht/kg |
| 3 | Nitrogen gas (Tank size 6 cubic, pressure 2,000 psi) | 300 | Baht/tank |
| 4 | Carbon dioxide gas (Tank size 6 cubic, pressure 2,000 psi) | 1,500 | Baht/tank |
| 5 | Spe-ed matrix | 13,910 | 750 g/baht |
| 6 | Electricity | 4 | Baht/unit |

            In the cost of crude bio-oil with Equation 4.3, it was found that the material cost for crude bio-oil production consisted of oil palm shell cost, activated carbon commercial grade, and nitrogen gas. The cost will be the electrical energy used in microwave pyrolysis. The above costs for the product of crude bio-oil in each microwave pyrolysis can be shown in Table 4.14

**Table 4.14** Production cost of crude bio-oil from the microwave pyrolysis process

| Temp (ºC) | Ratio (OPS: AC) | Time (min) | Crude bio-oil (ml) | Cost of raw material (Baht/batch*) | | | Total Electricity cost (Baht/batch) | The total cost of crude bio-oil (Baht/batch*) | Cost of crude bio-oil (Baht/ml) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | OPS | AC | $N_2$ | | | |
| 700 | 80:20 | 30 | 116 | 1.04 | 2.0 | 1.9 | 2.38 | 7.32 | 0.06 |
| 700 | 70:30 | 40 | 94 | 0.91 | 3.0 | 2.4 | 2.86 | 9.17 | 0.10 |
| 700 | 70:30 | 30 | 95 | 0.91 | 3.0 | 1.9 | 2.38 | 8.19 | 0.09 |
| 700 | 80:20 | 30 | 107 | 1.04 | 2.0 | 1.9 | 2.84 | 7.78 | 0.07 |
| 700 | 70:30 | 40 | 98 | 0.91 | 3.0 | 2.4 | 4.74 | 11.05 | 0.11 |
| 700 | 70:30 | 30 | 112 | 0.91 | 3.0 | 1.9 | 3.05 | 8.86 | 0.08 |
| 400 | 80:20 | 30 | 31 | 1.04 | 2.0 | 1.9 | 1.17 | 6.11 | 0.20 |
| 400 | 80:20 | 30 | 33 | 1.04 | 2.0 | 1.9 | 1.45 | 6.39 | 0.19 |
| 400 | 70:30 | 40 | 33 | 0.91 | 3.0 | 2.4 | 1.57 | 7.88 | 0.24 |
| 400 | 70:30 | 30 | 48 | 0.91 | 3.0 | 1.9 | 1.27 | 7.08 | 0.15 |
| 400 | 80:20 | 40 | 56 | 1.04 | 2.0 | 2.4 | 1.06 | 6.50 | 0.12 |
| 400 | 70:30 | 30 | 44 | 0.91 | 3.0 | 1.9 | 1.16 | 6.97 | 0.16 |
| 700 | 80:20 | 40 | 123 | 1.04 | 2.0 | 2.4 | 3.05 | 8.49 | 0.07 |
| 550 | 75:25 | 35 | 88 | 0.98 | 2.15 | 2.15 | 2.94 | 8.22 | 0.09 |
| 400 | 80:20 | 40 | 48 | 1.04 | 2.0 | 2.4 | 1.42 | 6.86 | 0.14 |
| 550 | 75:25 | 35 | 84 | 0.98 | 2.15 | 2.15 | 2.52 | 7.80 | 0.09 |
| 700 | 80:20 | 40 | 116 | 1.04 | 2.0 | 2.4 | 3.05 | 8.49 | 0.07 |
| 400 | 70:30 | 40 | 30 | 0.91 | 3.0 | 2.4 | 1.53 | 7.84 | 0.26 |

**Note:** *1 batch (batch of production) = 500 grams

Table 4.14 The cost of crude bio-oil production was in the range of 0.06 - 0.26 baht/ml at the temperature 700 °C, the ratio of oil palm shell to activated carbon was 80:20 for 40 minutes. which produces the highest crude bio-oil content The production cost is 0.07 baht/ml. The cost of crude bio-oil production at this condition was used to calculate the production cost of bio-phenol with the supercritical fluid extraction with carbon dioxide; $scCO_2$ extraction. Therefore, the cost of producing bio-phenol is as follows:

1) Crude bio-oil production cost

2) Dispersant (spe-ed matrix$^{TM}$) It is used to absorb and disperse viscous crude bio-oil during the supercritical fluid extraction process

3) Carbon dioxide used in the $scCO_2$ extraction process

The cost of bio-phenol production is shown in Table 4.15. It was found that the cost of bio-phenol production from the $scCO_2$ extraction process studied was in the range of 82.16-108.93 baht/ml. It was found that the condition temperature was at 50 °C, pressure 400 bar, and extraction time 30 minutes. To extract the highest amount of bio-phenol and the production cost is 82.16 baht/ml. In this research, the production cost of bio-phenol by supercritical fluid extraction with carbon dioxide process is quite high and the extraction by this method was the amount yield of bio-phenol is not as high as it should be compared to the bio-phenol content in crude bio-oil analyzed by GC-MS. The extraction method was more pronounced than the extraction of bio-phenols. Therefore, the method of bio-phenol production by $scCO_2$ extraction is not suitable for bio-phenol extraction.

**Table 4.15** scCO₂ oil production costs and bio-phenol production costs

| Temp (°C) | Pressure (bar) | Time (min) | Crude bio-oil (ml) | Cost of raw material (Baht/batch*) | | | Cost of scCO₂ oil (baht) | scCO₂ oil (ml) | scCO₂ oil (baht/ml) | % of phenol | Phenol (ml) | Cost of phenol (bath/ml) | Cost of phenol (bath/ml) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Crude bio-oil | Spe-ed matrix seed | CO₂ | | | | | | | |
| 50 | 300 | 30 | 20.03 | 14.00 | 185.33 | 22.50 | 221.83 | 10.00 | 22.18 | 23.14 | 2.31 | 95.86 | 86.81 |
| 50 | 300 | 30 | 20.01 | 14.00 | 185.33 | 22.50 | 221.83 | 8.11 | 27.35 | | 2.85 | 77.75 | |
| 50 | 400 | 30 | 20.03 | 14.00 | 185.33 | 22.50 | 221.83 | 10.26 | 21.62 | 23.83 | 2.32 | 95.51 | 79.54 |
| 50 | 400 | 30 | 20.00 | 14.00 | 185.33 | 22.50 | 221.83 | 6.83 | 32.48 | | 3.49 | 63.58 | |
| 60 | 350 | 30 | 20.01 | 14.00 | 185.33 | 22.50 | 221.83 | 9.75 | 22.75 | 23.65 | 2.43 | 91.45 | 83.15 |
| 60 | 350 | 30 | 20.05 | 14.00 | 185.33 | 22.50 | 221.83 | 7.98 | 27.80 | | 2.96 | 74.85 | |
| 70 | 300 | 30 | 20.01 | 14.00 | 185.33 | 22.50 | 221.83 | 10.72 | 20.69 | 20.91 | 1.95 | 113.73 | 98.56 |
| 70 | 300 | 30 | 20.04 | 14.00 | 185.33 | 22.50 | 221.83 | 7.86 | 28.22 | | 2.66 | 83.39 | |
| 70 | 400 | 30 | 20.03 | 14.00 | 185.33 | 22.50 | 221.83 | 10.64 | 20.85 | 21.03 | 1.98 | 112.23 | 101.84 |
| 70 | 400 | 30 | 20.14 | 14.00 | 185.33 | 22.50 | 221.83 | 8.67 | 25.59 | | 2.43 | 91.45 | |

# CHAPTER 5
# CONCLUSION AND SUGGESTION

## 5.1 Conclusion

In this study, the microwave pyrolysis system for producing crude bio-oil and bio-char from palm oil industry waste material, oil palm shell. The microwave pyrolysis system consists of 4 microwave sources (magnetrons) and was designed, developed, and built by simulating the dispersion characteristics of microwave waves inside a reactor with width, length, and height equal to 0.22 m, 0.22 m, and 0.31 m. respectively, with a computer program based on the Finite Element Method (FEM). The system can measure temperature with a thermocouple and control the temperature inside the reactor with an automatic temperature control system and through the data collection into the computer through the RS485 port, including the electrical energy data used in the microwave pyrolysis experiment with a vapor, condensation system to return to a liquid in the form of crude bio-oil. When calibrating the built system with water. It was found that the average microwave power with two magnetrons on at a time was 896.2 watts, and the system power with four magnetrons on at the same time was 1,454.9 watts.

The study of the microwave pyrolysis process of oil palm shells with the developed system. For determining the conditions of crude bio-oil production to obtain the maximum yield of crude bio-oil with three factors or variables in the study: temperature (T) in pyrolysis (400 and 700 °C), oil palm shell to activated carbon ratios (OPS: AC; 70:30 and 80:20) and time (t) to pyrolysis (30 and 40 minutes). In the $2^k$ full factorial design experiment, the regression equation was used to predict the maximum percentage of crude bio-oil as shown in equation 4.2 with $R^2$ and $R^2$-adj of 89.54% and 82.22%, respectively.

It was found that the highest percentage of crude bio-oil produced from the system that was built and developed based on the prediction with equation 4.2, at the 95% confidence interval was 24.08%, at the variable temperature (T) level of 700 °C, the ratio of oil palm shell to activated carbon (OPS: AC) was 80:20, and the pyrolysis time (t) was 40 minutes. When repeating the experiment to confirm the prediction results at the above conditions, the mean crude bio-oil was 21.90% ± 0.26, which was 2.18% from the predicted target. The crude bio-oil obtained from the microwave pyrolysis process can be seen in two phases: the oil phase, dark black below the bottom of the measuring cylinder, and the aqueous phase a dark brown separating layer above the upper oil phase of the measuring cylinder. When

the two phases were separated and the chemical composition of the two phases of the bio-oil products was analyzed by GC-MS, the results analysis of the composition of the aqueous phase and the bio-oil phase were acetic acid and phenol. Considering the solid product, it is the oil palm shell that has undergone the microwave pyrolysis process. (Converted to biochar from microwave pyrolysis) found that biochar has better thermal properties compared to oil palm shell that has not undergone pyrolysis process and analyzed the morphological structure physical appearance, surface area diameter porosity, and pore volume instruments showed that biochar obtained by microwave pyrolysis It has higher properties compared to the raw material, but it also has inferior properties than activated carbon commercial grade.

The crude bio-oil from microwave pyrolysis system at the highest percentage at condition temperature of 700 °C, ratio of oil palm shell to activated carbon was $80:20$ and pyrolysis time of 40 minutes, it was extracted $scCO_2$. To study the chemical composition such as bio-phenol and other chemicals in $scCO_2$ oil. It was found that the experimental conditions were at the extraction temperature of 70 °C, the extraction pressure of 300 bar, the flow rate of carbon dioxide was 3.0 liters/minute, and the extraction time was 30 minutes, resulting in the highest percentage of $scCO_2$ oil 67.81%. $scCO_2$ oil was analyzed with a GC-MS analyzer, The bio-phenol content in crude bio-oil was decreased However, the acidic products not found in crude bio-oil were dodecanoic, n-Hexadecanoic, and octadecanoic, this was due to the selectivity extraction of the $scCO_2$ process.

The cost of crude bio-oil production (two phases are accounted for, the aqueous phase and the oil phase, which have similar phenol content) and the $scCO_2$ oil. Considering the cost of materials and electricity used in the production of both types of oil referring to the price as of 1 October 2021, it was found that the cost of crude bio-oil production was in the range of 0.07 - 0.25 baht/ml. It was found that at a temperature of 700ºC, the ratio of oil palm shell to activated carbon was 80:20, and the pyrolysis time was 40 minutes, resulting in the highest crude bio-oil content. The production cost is 0.07 baht/ml. The cost of crude bio-oil production at this condition was used to calculate the production cost of bio-phenol extraction with supercritical fluid extraction with the carbon dioxide process. It was found that a temperature of 50 °C, a pressure of 400 bar, and an extraction time of 30 minutes, resulted in the highest bio-phenol content. The production cost was 79.54 baht/ml.

**5.2 Suggestions**

1) If obtained bio-char from the microwave pyrolysis process is required, as activated carbon, the thermal and chemical activation processes are needed.

2) Other dispersants are required to reduce the cost of supercritical fluid extraction with carbon dioxide.

3) Oil palm shell may be directly used for bio-phenol extraction by carbon dioxide supercritical fluid process due to this process actives with the solid phase.

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# APPENDIX A



**Figure A1** Physical characteristics of OPS before grinding.



**Figure A2** Physical characteristics of OPS after grinding.



**Figure A3** Physical characteristics of activated carbon.

**Figure A4** Raw material grinding with automatic grinder.



**Figure A5** Raw materials dried in a hot air oven at 105 °C.



**Figure A5** U.S. Standard Testing Sieve

**Figure A6** Nitrogen gas



**Figure A7** Teflon cap for Quartz glass



**Figure A8** Quartz glass

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