

**VALORIZATION OF DISPOSABLE COVID-19  
PERSONAL PROTECTION EQUIPMENT  
THROUGH THE THERMO-CHEMICAL  
PROCESS**

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**FACULTY OF ENGINEERING  
UNIVERSITY OF MALAYA  
KUALA LUMPUR**

**2022**

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PERSONAL PROTECTION EQUIPMENT THROUGH  
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**RESEARCH REPORT SUBMITTED IN FULFILMENT  
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## ABSTRACT

Medical waste in the form of Personal Protective Equipment (PPE) has been in the rise in these days especially due to the pandemic hit in 2019. These surge in medical wastes skyrocketed as compared to previous years making it one of the wastes that had to divert our attention to treat it properly. Several attempts at treating it has been done such as incineration, landfill, chemical disinfection microwave and autoclaving but pyrolysis had been found out to be one of the viable options that is much greener than the others. Through pyrolysis a usable and beneficial product can be obtained in the form of hydrocarbon while ensuring the environment clean. The hydrocarbon which is the bio-oil obtained from the pyrolysis process had to be of good quality in order it to be compatible for substitution of petroleum-based oil. As such upgradation of the oil is also essential due to the volatile nature of the PPE. This is where the coconut shell/copra comes into play. Coconut shell can be also found abundant in Malaysia due high usage of coconut milk in households. With this opportunity, a co-pyrolysis process had been developed between PPE and CCS in this study. The experiment showed addition of coconut shell (CCS) to PPE for co-pyrolysis had decreased the yield of the bio-oil when compared to pure pyrolysis of PPE and CCS. This is due to the CCS being already a good feedstock itself by having high amount of hydrocarbon compound produced. The yield drop can be also explained due to the volatile nature of PPE and most of the compounds formed in gaseous state. However, from the HHV analysis, it has also been found there was significant increase in hydrocarbon compounds in co-pyrolysis product when compared to pure PPE. The amount of esters and other oxygenates also been removed from CCS due to synergistic effect making the final product of co-pyrolysis that has much better heating value at 20% when compared to PPE and 50% to CCS with much closer attribute

to the petroleum-based hydrocarbon. This study concludes that by having CCS introduced to PPE, the bio-oil yield had dropped but the quality of the bio-oil obtained of better quality.

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## ABSTRAK

Sisa perubatan dalam bentuk alat pelindung diri (PPE) semakin meningkat pada masa kini terutamanya disebabkan oleh pandemik yang melanda pada tahun 2019. Lonjakan bahan buangan perubatan ini menjadikannya salah satu perkara yang perlu mendapat perhatian kita untuk merawatnya dengan kaedah yang betul. Pelbagai usaha telah dilakukan seperti insinerasi, pelupusan di tapak, gelombang mikro, pembasmian kuman melalui kimia dan autoklaf tetapi kaedah pirolisis telah mendapat perhatian yang tinggi. Melalui pirolisis, produk yang berfaedah boleh diperolehi dalam bentuk hidrokarbon sambil memastikan persekitaran bersih. Hidrokarbon yang merupakan bio-minyak yang diperolehi daripada proses pirolisis mestilah berkualiti tinggi supaya ia serasi untuk penggantian minyak berasaskan petroleum. Oleh itu, peningkatan kualiti minyak juga penting disebabkan sifat minyak PPE yang mudah lesap. Di sinilah tempurung kelapa/kopra memainkan peranan yang penting. Tempurung kelapa boleh didapati dengan kuantiti yang tinggi di Malaysia kerana kebanyakan rumah tangga menggunakan santan untuk memasak. Dengan menggunakan peluang ini, proses ko-pirolisis telah dibangunkan antara PPE dan kelopak kelapa (CCS) dalam kajian ini. Kajian menunjukkan penambahan CCS kepada PPE untuk ko-pirolisis telah mengurangkan hasil bio-minyak jika dibandingkan dengan pirolisis tulen PPE dan CCS. Ini disebabkan oleh sifat CCS yang mempunyai jumlah sebatian hidrokarbon yang tinggi. Penurunan hasil juga boleh dijelaskan kerana sifat PPE yang mudah lesap telah bertukar menjadi bahan gas. Walau bagaimanapun, daripada analisis HHV, didapati juga terdapat peningkatan ketara dalam sebatian hidrokarbon jika dibandingkan dengan PPE tulen. Kandungan ester dan oksigenat dalam CCS telah hilang sepenuhnya kerana kesan sinergistik menjadikan produk akhir ko-pirolisis yang mempunyai nilai pemanasan yang lebih baik sebanyak 20% berbanding PPE dan 50% berbanding CCS dengan mempunyai ciri-ciri yang lebih

sama dengan hidrokarbon berasaskan petroleum. Kajian ini menyimpulkan bahawa dengan memperkenalkan CCS kepada PPE, hasil bio-minyak telah menurun tetapi kualiti bio-minyak yang diperolehi telah meningkat.

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## LIST OF SYMBOLS AND ABBREVIATIONS

CCS/CC	:	Coconut Shell / Coconut Copra
SMS	:	Spunbond Meltblown Spunbond
PPE	:	Personal Protective Equipment
PP	:	Polypropylene
PE	:	Polyethylene
PET	:	Polyethylene Terephthalate
PO	:	Polyolefins
PVC	:	Polyvinylchloride
PS	:	Polystyrene
PU	:	Polyurethanes
TG/TGA	:	Thermogravimetric Analysis
GC-MS	:	Gas Chromatography Mass Spectrometry
HDPE	:	High-Density Polyethylene
LDPE	:	Low-Density Polyethylene
HHV	:	Heating Value
DTG	:	Derivative Thermogravimetric

## CHAPTER 1: INTRODUCTION

### 1.1 Background

As of one of the commodities, energy producing fuels such as crude oil or coal are driving force for the development of the world economy. With increase in energy demand over the years, finding alternative energy source such as renewable sources have become mission statement of most of the countries in the recent years (Cristina Rezende Lopes & Tannous, 2020). This need becomes even more accelerated due to the Coronavirus Outbreak in 2019 (COVID-19) as countries became even more environmentally conscious and use the situation as a steppingstone to further develop sustainable energy sources.

Like sunlight, wind and water, researchers have identified biomass as a sustainable, renewable and eco-friendly energy source (Azeta, O.Ayeni, Agboola, & B.Elehinafe, 2021). Wastes from agriculture are regarded as a viable energy generation source to meet the growing demands of energy consumption and addressing fossil fuel depletion and environmental degradation (ADENIYI et al., 2019). Malaysia, one of the Southeast Asian countries, has established targets for the application of fuels generated from agricultural wastes as an alternative source of energy (Abnisa & Wan Daud, 2014). From the previous studies conducted on Malaysian agricultural production, coconut and paddy plantations are among the major agricultural crops grown here (Shafie, Mahlia, Masjuki, & Ahmad-Yazid, 2012). The solid wastes from these two types of crops are produced in large quantities and yet they possess no value. Thus, by utilizing the biomass, these wastes can acquire significant value while also contributing to the reduction of environmental hazard (Balasundram, et al., 2017).

With the recent hit by COVID-19 outbreaks, nations were affected heavily by many challenges. The disease sees a continual increase in number over the years and yet to reside and these has resulted in a series of health, socio-economic and environmental problems (Mofijur, et al., 2021). Consequently, the health care industries begin to output significant number of medical wastes which warrants a proper disposal method, and this became another hurdle the nations had to face with. Taking Wuhan as an example, the generation of medical wastes sky-rocketed from 3.64 to 27.32 kg/day per one thousand persons since the outbreak of COVID-19. Most of the wastes are contributed by the personal protective equipment (PPE) such as protective suits, facemasks, nitrile gloves, safety goggles and testing kits (Mofijur, et al., 2021). As mentioned before, the disposal of medical wastes is a matter that must be handled carefully especially due to their toxicity (Moreira & Günther, 2013).

Several technologies have been explored and developed to tackle the disposal issue including incineration, landfill, chemical disinfection, autoclaving, microwave, plasma and pyrolysis (Maruful Hoque & Tauhid Ur Rahman, 2020). As the most conventional and economically sound solution, incineration has been favourite technique of many countries. Despite the advantage in economic standpoint, the environmental effect such as ashes with toxic metals and poisonous gases generation cannot be disregarded and it also poses a serious threat to human health (Makarichi, Jutidamrongphan, & Techato, 2018). Another widely used disposal method is the landfill disposal method due to its easy operation and low capital cost. However, the side effects such as large land occupation, toxic gases release and the risk of virus spread cannot be overlooked. This puts a lens on the other four techniques that are less conventional and yet could be potentially better for the environment. Among these four is pyrolysis which has the ability to convert various wastes into a valuable fuel of chemical while obtaining higher recovery

efficiency and lower environmental impact (Niu, et al., 2022). Pyrolysis is a thermochemical conversion method which converts either organic or inorganic matter into various products including biochar, condensable vapours (*i.e.*, bio-oil), and permanent gases. Liquid biofuels are considered the most promising option for substituting fossil fuels among all the other products of pyrolysis (Mo, et al., 2022).

Many varieties of biomass (sewage sludge, straw husk and sawdust etc.) and reactors (fixed bed reactor, fluidized bed reactor and TGA etc.) had been researched under various conditions (temperature and heating rate etc.) (Mo, et al., 2022). However, biomass introduces difficulties such as relatively low in energy density, seasonal supply fluctuation and collection difficulties that limits pyrolyzate quality and pyrolysis scale (Guo & Bi, 2015). To mitigate this, co-pyrolysis with plastics such as polyvinylchloride (PVC), polyurethanes (PU), polyethylene terephthalate (PET), polyolefins (PO) and polyethylene (PE) is a promising technology to obtain energy-rich value-added quality liquid products (Dash & S., 2015), (Abnisa & Wan Daud, 2014). These are the typical plastics that usually medical wastes are also made of. To enhance the product quality of the co-pyrolysis process, both biomass and plastics are co-processed via synergistic interactions. The induced synergistic effect is the prime factor for obtaining superior quality oil with high yield liquid hydrocarbons (Suriapparao, Kumar, & Vinu, 2022).

As to employ both biomass and plastics for the pyrolysis process, this study focuses on co-pyrolysis with coconut copra and the medical waste (PPE). In over ninety countries, coconut wastes are one of the most abundant biomasses found with a global output of 62.5 million tons per year (Cristina Rezende Lopes & Tannous, 2020). In countries like India, coconut shells are also used as charcoal as it burns with significantly lower emission of carbon dioxide and methane. Furthermore, coconut shells are suitable for



pyrolysis process because of its lower ash content and higher volatile matter content (Balasundram, et al., 2017). A study was conducted by (Su, et al., 2021) on analysing commonly used biomass to show the differences in the properties of medical wastes and other biomass materials shows that medical wastes is one of the promising feedstocks for energy recovery. This is proven by its high hydrogen content and relatively high carbon content. Besides, medical wastes also possess high volatile matter which works in favour due to its high yield in bio-oil generated during pyrolysis process. Thus, by employing co-pyrolysis method on coconut copra and medical wastes (PPE), a high quality and yield of bio-oil can be expected which is intention of this study to find out.

## **1.2 Problem statement**

As an alternative to petroleum fuels which has been many researchers focus nowadays, biofuel is considered one of the potential alternatives. As such, due to its high water and oxygen content in bio-oil, it comes with disadvantages of being unstable, corrosive, viscous and of a low-energy fuel-value. It is without a question, improvement to the bio-oil through necessary techniques are imperative. It is possible to obtain high-grade products by incorporating a higher hydrogen to carbon ratio ( $H/C_{eff}$ ) co-reactant (Engamba Esso, et al., 2022). This can be achieved by introducing plastic materials which has been found containing high number of carbon chains.

Recently, after the pandemic hit, as discussed above, there is huge surge in PPE usage. Many disposal methods had been explored and most of them are somehow eject harmful effects into the environment. To combat this issue, researchers had been finding ways to dispose the waste material in the most environmental way possible. Pyrolysis has been a topic that frequent in the current research landscape as it has very little to none effects to the environment. Plastic material from the PPE such as Spunbond Meltblown Spunbond

(SMS) that contains Polypropylene (PP) are being explored as the feedstock for the pyrolysis process. However, to produce a better-quality bio-oil, PPE alone would not suffice. As such, methods such as co-pyrolysis that combines different materials to produce superior quality product had to be employed.

Currently, numerous researchers are investigating the co-pyrolysis process in combination of plastics and organic materials. The main reason is due to the synergistic effect that allows the feedstocks to be converted into higher quality biofuels (Shahdan, Balasundram, Ibrahim, & Isha, 2022). This also allows to produce bio-oil in higher yield. In one of the examples, research conducted by (Niu, et al., 2022), co-pyrolysis of biomass and waste tire by introducing waste tire material into wheat straw and moso bamboo showed positive synergy on liquid production. Another research conducted by (Suriapparao, Kumar, & Vinu, 2022), showed by co-pyrolysis of PET bottle waste and rice husk increases the heating value due to the increase in 34-36 MJ/kg. This shows that there are several other advantages that can be reaped if co-pyrolysis of plastic and biomass are explored more.

There are many possible combinations for co-pyrolysis method and as discussed above mostly in combination of biomass and plastic. However, there were no specific research had been done to explore the co-pyrolysis of Coconut Copra (CC) and medical waste (PPE) which in this case Polypropylene (PP) found in SMS. This paper intends to explore the properties of the above-mentioned co-pyrolysis while addressing the fundamental issue of proper PPE disposal while producing a useful by-product.

### 1.3 Research Objectives

1. The main objective of this study is to produce bio-oil through pyrolysis of plastic waste. This will be achieved by:
  - a. To study the decomposition of Coconut Shell and Personal Protective Equipment.
  - b. To investigate the effect of co-pyrolysis of Coconut shell and Personal Protective Equipment and bio-oil production yield.
  - c. To analyse the heating value of bio-oil produced.

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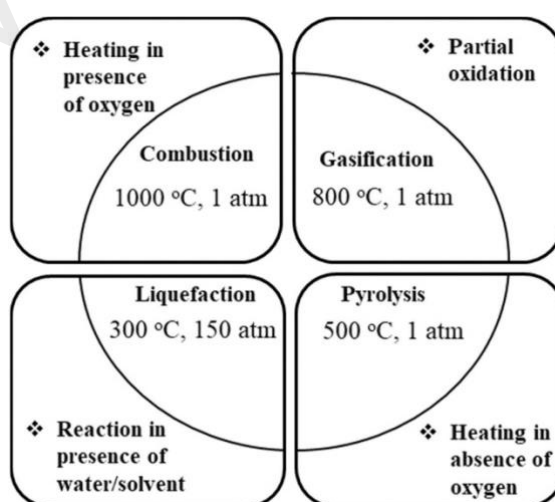
## CHAPTER 2: LITERATURE REVIEW

### 2.1 Introduction

Non-renewable resources such as coal and oil had been the centre of large-scaled production that contributed large number of harmful substances such as carbon dioxide, sulphide and large particle dust. This has led to a series of ecological and environmental problems such as large-scale haze and rise in global temperature that hinders the sustainable development of economy and society. Biomass, as the only carbon resource, has the potential to substitute fossil fuel due to its large yield, strong sustainability, low cost, high organic content and low greenhouse gas emissions (Qiu, et al., 2022). Besides, due to its abundance it can be considered renewable carbon source. As biomass varies according to regions, mostly it is made up of lignocellulose which contains cellulose, hemicellulose and lignin. The thermal decomposition starts with hemicellulose, followed by cellulose and lignin as the temperature increases due to the crystallinity of the components (Shahdan, Balasundram, Ibrahim, & Isha, 2022). Through the means of thermochemical, biomass can turn many potential feedstocks into usable products such as bio-oil that can act as fuel, biochar which can be used as fertilisers, and gaseous fuels. Bio-oil has been identified a very good substitute for fossil fuel as it has several merits that can be warranted such as high energy density, easy storage and transportation. It can be used to power engines, boilers and even aviation transport through further refinement. The aldehyde and ketones content in some bio-oil can be transformed onto variety of high-value added derivatives due to their active chemical properties (Qiu, et al., 2022).

## 2.2 Thermochemical Technologies

There are several types of promising thermochemical platforms for processing biomass feedstocks such as combustion, gasification, hydrothermal liquefaction and pyrolysis. The major differences in operating conditions of these process can be summarised as the figure 2.1. In combustion process, biomass is decomposed in presence of externally supplied oxygen to convert the trapped chemical energy into heat via exothermic reaction. The generated heat energy is then utilised for commercial use. However, the major disadvantages of this process are its high-level pollutant ejection and low process efficiency (Suriapparao & Tejasvid, 2022). Furthermore, gasification is a partial oxidation process that produces synthetic gaseous fuel like syngas ( $\text{CO}+\text{H}_2$ ) when subject to temperature range of  $700\text{-}1000\text{ }^\circ\text{C}$ . Burning gaseous fuel is much more efficient and well-controlled and the equipment to process it can be also integrated with industrial process for power generation and chemical production. Although it is one of the most efficient platforms, it requires a high capital investment for plant design. Besides, the storage and transportation of gaseous state is much more complex and costs higher compared to of solids and liquids.



**Figure 2.1: Thermochemical valorisation platforms (Pandey, Bhaskar, Stöcker, & K. Sukumaran, 2015)**

Pyrolysis is a process that is conducted in absence of oxygen in temperature range of 400-600 °C. This process produces 3 types of products namely, gas, char, and bio-oil which are very different outcomes compared to combustion and gasification. The temperature range to produce the product varies greatly with the types of feedstocks supplied to it. However, the pyrolysis still will take into effect as long it is conducted in high temperature range. Pyrolysis can be further classified into slow, fast and flash pyrolysis which depends on the heating rate, temperature, residence time, product requirement and reactor type (Suriapparao & Tejasvid, 2022).

#### *Slow pyrolysis*

Also known as carbonization, slow pyrolysis occurs at relatively low temperature with slow heating rate and long solid residence. This process produces about 15% higher bio-char yield compared to bio-oil due to longer retention time and relatively lower heating rates which causes the formation of more carbonaceous solids (Azeta, O.Ayeni, Agboola, & B.Elehinafe, 2021). Furthermore, low temperature (200-300 °C) and heating rate (0.1-5 °C) with long residence time (hours) of slow pyrolysis results in high yield of char rather than the bio-oil (Suriapparao & Tejasvid, 2022).

#### *Fast pyrolysis*

Fast pyrolysis is favoured for its great potential in industrial fuel and transport fuel application in which the technique emphasizes on maximizing the bio-oil yield of high quality and quantity. This process requires very high heat transfer and heating rates that needs finely ground feedstocks, controlled temperature and rapid cooling of the pyrolysis vapour to give bio-oil. The temperature measured during the process through oven temperature instead of biomass temperature usually leads to overestimation of actual

biomass heating rate and denies the temperature gradient across the sample (Siengchum, Isenberg, & Chuang, 2013). Through this, yields the bio-oil which has the components that are complex, with characteristics of high oxygen content, high water content, low calorific value, strong corrosivity, high viscosity, poor stability and insolubility in traditional liquid fuel which suggest bio-oil generally can be used as low-grade fuel (Qiu, et al., 2022). However, (Wang, et al., 2022) contradicts by saying the bio-oil products gives content that has high carbon and hydrogen contents especially in plastics wastes and poses some properties very similar to petroleum fuel (especially diesel) (e.g., high HHV, low oxygen and low water content, similar O/C and H/C ratios, cetane index, etc.). This shows, bio-oil obtained varies greatly with the feedstocks and condition supplied to the pyrolysis process.

#### *Flash pyrolysis*

This process is carried out through very short contact times at temperatures too high, high heating rates with small particle sizes of biomass of no more than 200  $\mu\text{m}$ . Higher heating rates of 1000-10,000  $^{\circ}\text{C}/\text{s}$  and shorter residence times ( $<0.5$  s) of flash pyrolysis yields bio-oil of up to 75-80 wt% due to its high release of gaseous products during the process. In one of the cases, a study was done on characteristics and thermal degradation behaviour of coconut pulp alongside rice husk, it was observed particle size has little to no effect on the pyrolysis process. It resulted in high yield in bio-oil of coconut pulp regardless of the particle size (Azeta, O.Ayeni, Agboola, & B.Elehinafe, 2021).

Thermogravimetric (TG) analysis is used to gauge the thermal decomposition and its reaction kinetics by measuring the remained mass of material which in this case the biomass as a function of time and temperature. This tool is also used often in assessing the thermal stability of various materials and their mixtures (Abbas-Abadi, Van Geem,

Hossein Bazgir, & Ghadiri, 2021). Numerous literatures recommend important procedures in two aspects, physical property (e.g., particle size) and operational conditions (e.g., sample mass, and heating rate). This statement is further explained by (Wang, et al., 2022) by categorizing the process as biomass pre-treatment. The author also added ash, moisture and hardness plays significant role for the pyrolysis process. Interpretation and calculations of kinetic parameters could end in error if the thermogravimetric is applied inadequately.

In (Cristina Rezende Lopes & Tannous, 2020) paper, the author found several literatures that agrees on applying small size particle (lower than 0.51 mm), but there are other literatures that did not state the diameter standard applied. In another paper, the author (Qiu, et al., 2022) mentioned when the particle size decreased from 1.5 mm to 0.3 mm, the bio-oil yield by pyrolysis increased. The author (Garg, Anand, & Kumar, 2016) conducted a study on gum seed as raw material by crushing its particle size into 0.4 mm, 0.6 mm, 0.5 mm and 1.0 mm and pyrolyzed at 500 °C. The study result shows, when the particle size increased, the gas yield decreased from 37% to 29%, the coke yield increased from 18% to 25.8% and the liquid yield decreased. By experimenting with olive and grape residue as feedstock at different particle size (0.4 ~ 2 mm), (Encinar, Beltrán, Ramiro, & González, 1997) found out with increasing particle size, the furfural (ff) yield increases and reaches the maximum at 2mm particle size. This phenomenon can be explained from the mass transfer perspective. The smaller biomass particles are conducive to heat transfer between the heating medium and biomass and accelerate the decomposition rate of biomass. Thus, the smaller biomass particles are advantageous to improve the yield of bio-oil (Qiu, et al., 2022).



## 2.3 Pyrolysis of Plastics

Plastics as discussed above had been known as the petroleum product. It has been gaining a lot of traction in many industries mainly due to its excellent properties that can easily cater them. Though it is widely used, the consequences to the environment due to difficulty in disposing should be ignored. Plastic wastes cause accumulation in the environment may cause clogging of drains and health issues. Besides, medical wastes which has plastic as one of the main components seen skyrocketed in accumulation in recent years due to the pandemic. Generally, the medical wastes contain plastics in the form of polyvinylchloride (PVC), polyurethanes (PU), polystyrene (PS), polyethylene terephthalate (PET), polypropylene (PP), polyolefins (PO) and polyethylene (PE) which are all considered as ideal pyrolysis feedstocks. Furthermore, the medical wastes are also great for energy recovery as they have the second-highest hydrogen content and relatively high carbon content (Su, et al., 2021). (Su, et al., 2021) in their paper also mentioned medical wastes possess third-highest calorific value and second-highest volatile matter which allows for higher bio-oil yield as illustrated in the figure 2.2 below. Since medical wastes constitute of many different types of plastics, these plastics can be analysed individually to understand their properties better.

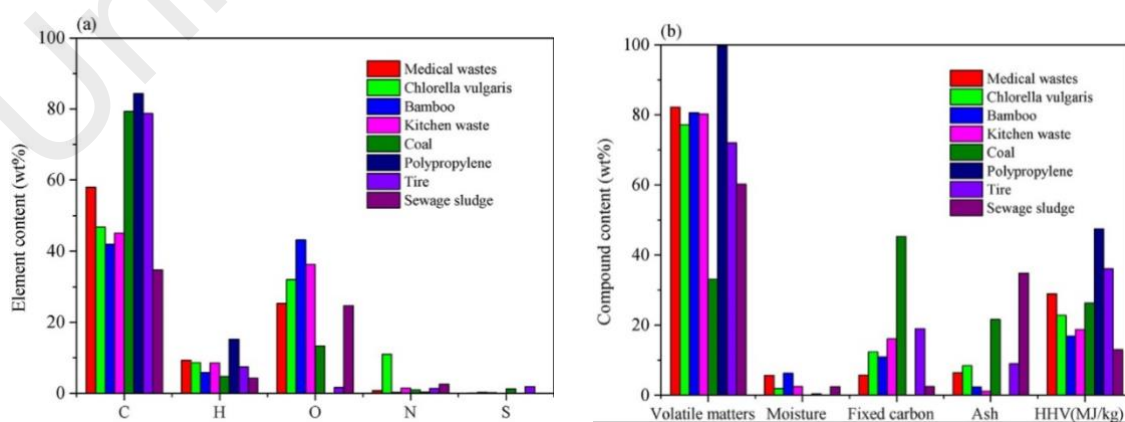


Figure 2.2: (a) Elemental and (b) proximate analyses of medical wastes and other materials

### *Polyethylene terephthalate (PET)*

PET is a lightweight plastic consisting of polymerised  $C_{10}H_8O_4$  monomers and it is largely used due its high-pressure resistance. High usage of this material will damage the environment. To dispose these wastes sensibly, the researchers explored through pyrolysis process. In a paper written by (Jahirul, et al., 2022) the author mentioned about a study conducted on pyrolyzed PET in a fixed-bed reactor at 500 °C pyrolysis temperature and a heating rate 10 °C/min using nitrogen as a carrier gas. In the experiment, the product yields 52.13% gas, 39.89% liquid and 8.98% solid char. Similarly, the experiment repeated by another author with gaseous yield of 76.9%, 23.1% liquid and no observed char. Due to the low volatile content of 86.75%-91.75% in the PET, the liquid yield is reduced.

### *High-density polyethylene (HDPE)*

HDPE consists of long polymer chains with low amounts of branching and high degree of crystallinity, which leads to a higher strength compared to LDPE. Since HDPE contains higher number of volatile compounds which amounts to 98.57% to 99.97% by weight, a high yield of liquid expected. A study was conducted by (Kumar & Singh, 2011) where the HDPE pyrolyzed at temperatures varying from 400-550 °C in a semi-batch reactor. The results shows that 79.08% high oil yield and 14.75% gaseous product obtained at 550 °C. However, at range of temperature of 500 °C to 550 °C, it was observed there was significant wax formation. Another study mentioned by (Jahirul, et al., 2022), studied pyrolysis of HDPE in lower temperature range of 300 °C to 400 °C to investigate the char production. The study showed the oil obtained was at maximum at 80.88% and the char obtained was significantly higher at 33.04% at 300 °C. When the temperature

increased to 400 °C, the solid char production was only at 0.54%. At high temperatures, the HDPE was observed to produce lesser oil and higher number of gaseous products.

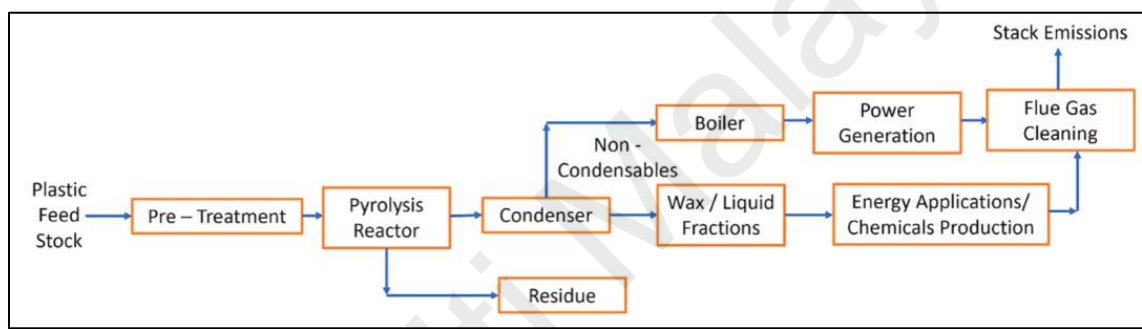
#### *Low-density polyethylene (LDPE)*

Compared to HDPE, LDPE has higher branching which reduces intermolecular forces, hence the hardness and tensile strength. Several recent studies had reported high oil yield obtained from LDPE pyrolysis. (Jahirul, et al., 2022) mentioned in their paper, a study about LDPE pyrolysis in a batch reactor at 550 °C was conducted gave results of 93% of oil yield with low amounts of solid char and gaseous products. The oil yield, however, was observed to decrease when the temperature of pyrolysis reduced to below 350 °C. The author mentioned two studies conducted on this matter by Aguado et al. and Uddin et al. at temperature 450 °C and 430 °C and both recorded oil yields of 76.5% and 74.7% respectively. Thus, with average temperature 500 °C, high oil yield can be obtained for LDPE.

#### *Polypropylene (PP)*

Polypropylene consists of saturated polymer with linear hydrocarbon chains. Several studies had been conducted on pyrolysis of polypropylene to analyse the characteristics and product yield. In the study mentioned by (Jahirul, et al., 2022), Demirbas et al. conducted the pyrolysis on PP in a batch reactor and obtained 49.6% gas, 48.8% liquid and 1.6% char. Similar to HDPE, the lower the pyrolysis temperature, the higher the oil yield observed. This is further solidified by the study conducted by Fakhrohoseini and Dastanian where they observed temperatures over 500 °C reduce oil production and increase gas production while char production remained insignificant.

Generally, PPE is made from Spunbond Meltblown Spunbond (SMS), which is a trilaminar non-woven fabric. This material consists of 3 layers where the bottom most layer being the spunbond PP layer followed by meltblown PP middle layer and finally spunbond PP top layer. As papers related to this material are scarce, the closest related material that can be discussed is polypropylene. Thus, moving forward this paper will relate the PPE to PP for ease of discussion. As discussed above, PP and many other plastics make great feedstocks and the figure below illustrates the current pyrolysis treatment for the plastic wastes done.



**Figure 2.3: Block diagram representing pyrolysis process. (Kartik, et al., 2022)**

## 2.4 Pyrolysis of Biomass

Biomass can be considered a significant energy source that can be tapped into. As discussed above there are many ways the energy can be harnessed from biomass and one of the cleanest ways is by using pyrolysis. Generally, they make a great feedstock for energy production due to their massive variety. However, due to differences of composition and structure, the pyrolysis characteristics of biomass raw materials are bound to be affected thus a carefully process of sifting through to select the best is important. In a study done by (Balasundram, et al., 2017) where pyrolysis of rice husks and coconut copra were observed. The author studied mainly on the volatile matter of

biomass as it can be further condensed into pyrolysis oil during pyrolysis. The rice husk was observed to have higher moisture content (6.7%) compared to coconut copra at 6.1% and this has translated in coconut copra yielding more volatile matter at 75.7 wt% while 55.9% for the rice husk. Therefore, the author concluded coconut copra will be able to yield more pyrolysis oil than rice husk. Similarly, (Qiu, et al., 2022) compiled many research on pyrolysis of biomass. In one of the study, wood raw materials had been found able to yield organic liquid yield highest while water and gas yield are the lowest. Due to large number alkali metals in agricultural biomass catalysing the pyrolysis of lignin, the yield of organic liquid produced by agricultural residues is the lowest. Another study mentioned in the same paper is by Mante et al. where the author studied the bio-oil from biomass raw materials (woody: pine and cypress, pine and hybrid poplar; switchgrass; agricultural residue: corn straw; forest residue: pine bark) by catalytic pyrolysis. The results obtained from bio-crude oil showed significant gaps in between the feedstocks such as differences in product distribution, aromatics, selectivity and physicochemical properties. This implies that different feedstocks produce different products. Furthermore, the studies also inform the O/C ratio in biomass plays an important role in producing gas-phase volatiles while the H/C ratio is conducive to obtain light aromatic hydrocarbons or gaseous hydrocarbon substances. The higher the volatile content, the more the bio-oil yield (Qiu, et al., 2022).

Another parameter for good pyrolysis in biomass is the ash content. The metal contents such as K and Ca in the ash can improve the heating rate of the reaction system during pyrolysis. However, there will be reduction in bio-oil yield if the ash content is too high because of the secondary cracking of pyrolysis vapor by the ash. As the example by (Balasundram, et al., 2017) illustrated, the presence of ash in biomass will tend to affect the overall yield of volatile matter. In the study conducted by the author, the high ash

content (17.1%) in rice husks has the lower yield of volatile matter compared to coconut copra which has lower ash content (0.6%) yielded higher volatile matter. As proposed by Chen et al., the concept of  $H/C_{eff}$  reveals lignocellulosic biomass with  $H/C_{eff} < 1.0$  belongs to hydrogen-deficient biomass and is difficult to convert into high quality bio-oil. Any feedstocks that have  $H/C_{eff} > 1.0$ , which have high hydrogen and low oxygen content will be able to yield high quality liquids. Furthermore, biomass is typically composed of higher number of aliphatic hydrocarbon structures and oxygen-containing functional groups but fewer condensed aromatic rings. The high atomic ratio of O/C enables any units related to oxygen bond are easy to break and form gaseous volatiles. During the pyrolysis process, the removal of H and O elements is easier than of C element due to the oxygen-containing functional groups (carbonyl and carboxyl) in the biomass are removed at a lower temperature. This is the very same reason why bio-oil has high polar components (phenols) and high content of CO, CO<sub>2</sub> and H<sub>2</sub> in pyrolysis gas (Qiu, et al., 2022). Besides, (Zhang, Liu, Yin, & Mei, 2013) mentioned higher fixed carbon in biomass could be a function of volatile matter. This is explained by the study conducted by (Balasundram, et al., 2017) where the rice husks with higher fixed carbon (20.3%) yielded lower amount of volatile matter compared to coconut husks that has lower fixed carbon. The author also mentioned another study reported high fixed carbon in biomass indeed increases the char yield and eventually decreases the liquid yield. Therefore, feedstocks with low fixed carbon and high O/C atomic ratio will produce higher amount of bio-oil.

Besides, there are also several caveats of biofuels derived solely from biomass such as low biofuel yield, high oxygen content, high moisture content, high viscosity, corrosive and thermally instable for long storage. As previously mentioned, the high oxygen and moisture content tend to reduce the heating value of the product (i.e., bio-oil) which

inhibits its potential as the replacement fuel for the commercial use as transport fuel which has heating value between 45 and 47 MJ/kg. Furthermore, the bio-oil from biomass has the property of increasing in viscosity as it ages which prevents it from long storage which is crucial for commercial use. The bio-oil derived from biomass is also corrosive in nature at pH around 2 to 3 while conventional petroleum has pH of around 7 (Shahdan, Balasundram, Ibrahim, & Isha, 2022). Thus, upgradation of bio-oil is crucial to reap its benefits.

In summary, both biomass and plastics like polypropylene in PPE has its own merits and disadvantages. These two feedstocks can complement each other to create an even better product. In this case, pyrolyzing plastic alone will create certain problems such as formation of wax or the quality is not good enough to use as biofuel. On the contrary, plastics like PP makes an excellent hydrogen donor when it is subjected to co-pyrolysis with biomass. When combined, the quality and the yield of the product which is bio-oil will increase. Further explanations of the co-pyrolysis are explained as follows.

## **2.5 Co-pyrolysis**

Co-pyrolysis is a simple and practical thermochemical technique as it does not require any adjustment from the typical individual pyrolysis (Engamba Ezzo, et al., 2022). When two or more components interact to produce an effect greater than individual pyrolysis, the process is subjected to synergistic effect (Kartik, et al., 2022). Due to synergistic effect, the yield, product and process characteristics of the process can differ from the single feedstock conversions. When the experimental value is different from the additive value, the synergistic or interactive effects will come into play which may promote or inhibit the process depending on whether the experimental value is greater or less than the additive value (Engamba Ezzo, et al., 2022). This effect is the main

contributor for improving oil quantity and yield as co-pyrolysis of biomass and plastics which able to transfer the hydrogen to surplus oxygen in biomass species by free radical interactions (Kartik, et al., 2022). This process has been experimented with various combinations such as between organic compounds (i.e., biomass) itself, between plastics (i.e., polyethylene, polypropylene, HDPE, LDPE) itself and cross-linking between biomass and plastics. The process of co-pyrolysis of biomass with other compounds can be affected by various attributes. The chemical attribute such as the interactions of their mineral compounds and physical attribute such as plastic melting can affect the pyrolysis products and, in some cases, reduce the rate of degradation. The mineral fillers and some pigments in plastics such as talc, calcium carbonate, kaolin, titanium dioxide, etc. can be effective in the pyrolysis process through the interaction with mineral compounds of biomass (Abbas-Abadi, Van Geem, Hossein Bazgir, & Ghadiri, 2021).

#### *Co-pyrolysis of biomass and plastics*

Various co-pyrolysis process between waste feedstocks and plastics had been seen effective due to their ability to produce fuel-based products and chemicals. Being one of fourth largest energy system after coal, oil and gas, biomass is the most prominent renewable energy. Despite being an abundant resource, the bio-oil extracted contains oxygen to extent of 60% in form of aldehydes, ketone, esters, alcohols and water. However, the high oxygen content causes a drop in calorific value, corrosiveness, instability, viscosity and high ash content which are vital in producing quality biofuel. These main caveats can be addressed by several ways mainly through techniques like hydrogenation, hydro-deoxygenation, steam reforming, molecular distillation that plays the role of upgrading the oil. A more economical method would be to use the co-pyrolysis method between biomass and plastics as involves hydrogen transfer during pyrolysis by eliminating the need for high energy input and high-pressure hydrogen handling (Kartik,



et al., 2022). The high hydrogen content in the plastics will be able to facilitate by inducing oxygen deficiency during co-pyrolysis with biomass which results in oil quality and quantity improvement.

Through several studies conducted on co-pyrolysis process, it has been found out there was increase in biofuel yield when biomass is paired with plastics. (Hassan, Lim, & Hameed, 2019) conducted a study on sugarcane bagasse and HDPE, able to determine there was 55% increase in biofuel production in co-pyrolysis compared to pyrolysis of bagasse alone. This is possible due to synergistic affect when biomass paired with plastic the plastic act as hydrogen donor, helping the decomposition of biomass and improving biofuel yield and quality (Shahdan, Balasundram, Ibrahim, & Isha, 2022). (Abbas-Abadi, Van Geem, Hossein Bazgir, & Ghadiri, 2021) also found several related research that mentions the addition of polyolefins to biomass, oxygen content in the final products is reduced. This addition boosts the yield of liquid especially hydrocarbons and reduce the coke and water produced. (Abbas-Abadi, Van Geem, Hossein Bazgir, & Ghadiri, 2021) also conducted a study on co-pyrolysis of plastics and oak and was able to determine there were 30-13% produced char, 19-10% water and 26-16% gas reduction and increase in hydrocarbon liquids by 14-78% as indicated by (Table 2.1). Similarly, a study conducted by (Kartik, et al., 2022) on co-pyrolysis of waste wood chips and polypropylene proved it was beneficial in many ways. The calorific value of the product increased to 63.1% compared yield from wood chips alone at 39%. Hydrocarbon's main components, carbon and hydrogen were also found increased during the co-pyrolysis while the oxygen decreased. These studies solidify the advantages the co-pyrolysis between biomass and plastics poses.

**Table 2.1: The pyrolysis products of oak, plastics and their blends (1:1) wt/wt.**

Sample	Liquid (%)	Gas (%)	Char (%)	Water (%)	Hydrocarbon (%)	Oxygenated (%)
oak	25	26	30	19	14	86
PE	85	12	3	0	100	0
PP	81	17	2	0	100	0
PS	92	7	1	0	100	0
PE: Oak	53	21	16	10	78	22
PP: Oak	51	24	14	11	75	25
PS: Oak	60	16	13	11	75	25

One of the attempts to further improve biofuel quality is by using catalysts which involves the amount of oxygenates reduction in the biofuel. The oxygenates are compounds that contains oxygen which when pyrolyzed produces acids, alcohols, aldehydes, esters, ethers and furans. When large amount of these components exists in the biofuel, the oxygen content increases thus the heating value lowered resulting in lower quality of biofuel. This issue is addressed by introducing the catalysts which helps to reduce the activation energy of the reaction consequently increasing the reactivity. Some of the common catalysts used for pyrolysis are zeolite catalysts, silicoaluminophosphate (SAPO), alkali and alkaline earth metallic (AAEM) species, transition metals and other metal-based catalysts. Zeolite catalysts (ZSM-5) are most widely used in catalytic pyrolysis due to the presence of strong acid sites that make the catalysts selective towards desired products such as benzene, toluene, ethylbenzene and xylene (BTEX) (Shahdan, Balasundram, Ibrahim, & Isha, 2022). A study was conducted by (Zhang, Zhong, Xie, Liu, & Ruan, 2016) on corn stover biomass using a susceptor bed at a pyrolysis temperature of 500 °C. It was found, when the catalysts-to-biomass ratio (w/w) increased from 1:100-1:20, the gas yield increased while that of bio-oil yield decreased monotonically. During the process, the vapors passed through the catalysts bed diffuses through pores of catalysts and thereby converting the oxygenates into hydrocarbon. The increase in catalysts-to-biomass also increases the yield of aromatic oxygenates. In (Shahdan, Balasundram, Ibrahim, & Isha, 2022) paper, the author mentioned with presence of catalysts, co-pyrolysis of sugarcane bagasse and HDPE produced higher

yields of biofuel of 68.6 wt%, with 74.6% of hydrocarbons. The author also mentioned without the presence of catalysts, reported a lower biofuel yield, 63.7 wt% with hydrocarbon percentage of 37.9%. Considering all the positive effects the catalysts may warrant, it is still expensive and using it in large amount will not be economical. In (Engamba Ezzo, et al., 2022) paper, the use of catalysts HZSM-5 on co-pyrolysis of pine wood and PE was mentioned. It was found the catalysts did not change the interaction mechanism while it only reduced the intensity of the synergy due to the presence of lignin and hemicellulose. There were also no cross-over products formed during the process. In this case, the synergistic effect had negative impact as the interaction suppressed the formation of aromatics. This is in contrast with other authors that previously mentioned regarding the positive effects of catalysts. It can be concluded that by adding catalysts into co-pyrolysis process especially between biomass and plastics may not be deemed to have positive effect but in fact it could have adverse effect.

To recap this chapter, PPE as currently being one of the most prominent medical wastes had to be treated in a sensible way and most of the PPE were made from PP which is a type of plastics. There are many ways of disposing and pyrolysis could be one of the most beneficial ways to create energy while disposing the wastes in an environment friendly way. Since pyrolysis of plastic alone had been proven as lacking. As plastics have high hydrocarbon components in them, they are still subject to wax formation resulting in less quality of bio-oil. Similarly, biomass had also been discovered to be potential feedstocks. They are huge in number and open burning which is the popular option for disposal has been proven very harmful to the environment and pyrolysis is a great salvation for this issue. Biomass has much more variety in feedstocks and properties and each has distinguishing parameter that differentiates from each other. However, from analysis by various researchers as mentioned in this chapter the biomass can be easily

sorted out to get the best. The main parameters to be considered from the biomass are the volatile matter content, low fixed carbon, high O/C and low moisture content to yield the highest amount of bio-oil. Like the PPE, pyrolysis of biomass alone will still have certain downsides that prevents it to being petroleum fuel substitute. This is mainly because pyrolysis of biomass produces much less bio-oil than of others such as plastics due to their high char production. Biomass also produces bio-oil of high viscosity, high oxygen content and has much shorter shelf life to warrant it as good fuel oil. A method to devise upgradation of bio-oil is essential and this is where the co-pyrolysis plays an important role.

Co-pyrolysis is the process that uses synergistic effect between feedstocks to produce a better product. Numerous experiments had been done to experiment this process due to the vast availability of possible combinations. Many has experimented between different combinations of biomass itself and several studies also experimented on combinations of different types of plastics. However, combining both biomass and plastics had piqued many researchers interest due to the feedstocks way of complementing each other to produce better product. The high content of oxygen in the biomass is complemented by the PPE which can act as hydrogen donor and produces a higher yield and quality bio-oil. In this chapter, many findings had been discussed on how well the biomass and plastics can complement each other. The findings suggested when both are subjected to co-pyrolysis, hydrocarbon's components, carbon and hydrogen had been found increasing while the oxygen content reduced. This greatly improves the heating value which is essential to produce energy dense biofuel.

The pyrolysis process also had been discussed extensively in this chapter especially the types of pyrolysis to yield the highest amount of oil. Slow pyrolysis was found to

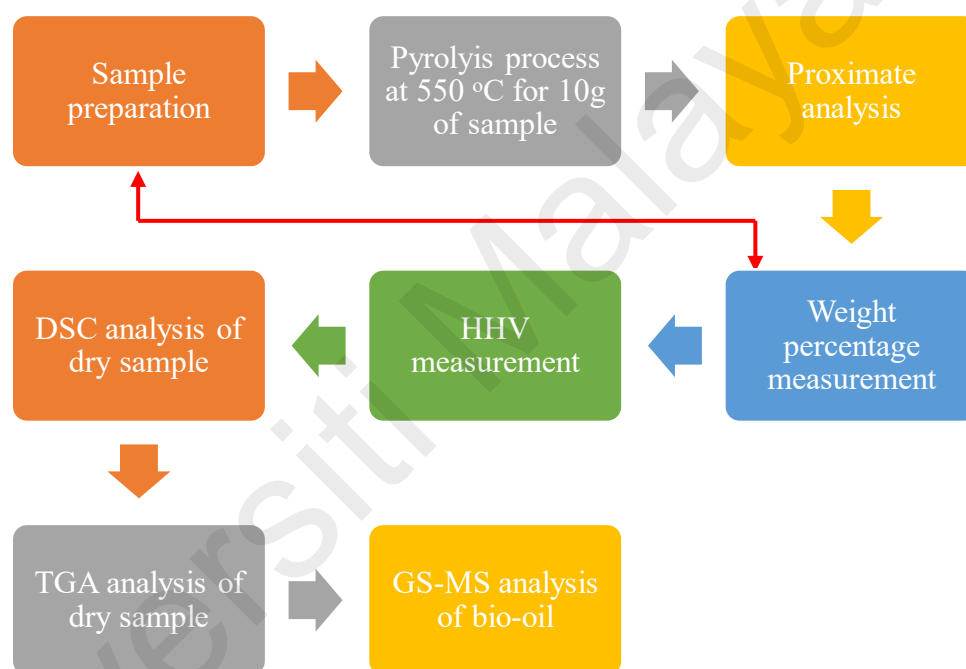
produce more char and this can be beneficial for studies involving char. Flash pyrolysis on the other had able to produce the highest oil yield but at much higher temperature of 1000-10000 °C. The equipment to handle such temperature are scarce and it is uneconomical to produce beyond the lab experiment scope. As such fast pyrolysis was the method found the best as it strikes the middle ground of the two. It can produce high yield of bio-oil while subjected to temperature between 300-600 °C.

The usage of catalysts also had been discussed for catalytic co-pyrolysis. Zeolite catalysts (ZSM-5) is the catalysts that had been getting a lot attention from the researchers. Studies had showed in some cases, the catalysts helped to decrease the temperature required for the pyrolysis but some showed there is little to no effect on the process. This is especially true for co-pyrolysis between biomass and plastics where studies had been proven it had the opposite effect due to negative synergy which ended in lower aromatics. Besides, adding catalysts also increases the cost of the whole process and thus co-pyrolysis without adding catalysts will be preferred.

From the studies that had been conducted on co-pyrolysis, there is a gap where co-pyrolysis between coconut copra and PPE had not been explored. The coconut copra had been proven to have low fixed carbon and low moisture content from the studies in this chapter. They are also abundant in number as in Malaysia we consume a lot of coconut milk for cooking purposes. Naturally, the coconut copra or shell becomes a huge waste that can be turned into potential source for co-pyrolysis. This process will help to reduce both medical and biomass wastes while producing useful energy products.

## CHAPTER 3: METHODOLOGY

The first phase of the experiment is to prepare the sample and conducting the pyrolysis. After taking the weight percentage of a sample, the first phase repeated again for the other sample as shown in the figure 3.1 below. When all the samples had been pyrolyzed, the samples are then prepared to be sent for lab analysis.



**Figure 3.1: Flowchart of the pyrolysis process**

### 3.1 Materials

As mentioned above the chosen feedstocks for the co-pyrolysis process are coconut copra and PPE. The coconut copra (CC) was obtained from a convenience shop which was disposed after the inner coconut flesh has been shredded off. Total of 4 halves of copra were obtained and broken down into smaller pieces using a hammer. To make the

sample free of flesh or husks, it was washed thoroughly to remove any unwanted content. The pieces were then left in the laboratory hot air oven at 105 °C to remove physisorbed moisture. Then, the pieces were further pulverized into powder form by using milling blender and sieved to obtain the average particle size of 150 µm. The samples were prepared to have at least 60 grams in total for three runs of 20 grams each to obtain average reading.

Preparation of PPE were much easier. Since these were part of the medical waste apron, it was simply cut into smaller pieces. However, due to its mass and density, the material was much lighter, so more of this material was needed to get 60 grams in total. The size cut was approximated about 0.5 mm each piece. Both feedstocks were stored in glass sample bottles to prevent any contaminations.

### **3.2 Experiment Setup**

Since Thermogravimetry analysis and Differential calorimetry were necessary to be conducted to analyse the initial composition of the feedstocks, there were three samples were prepared which are coconut shell powder, PPE and mixed coconut shell powder with PPE. The samples were then submitted to the designated labs for analysis.

The co-pyrolysis was then conducted at designated operating conditions in a pyrolysis reactor which in this case the re-modelled STERICOX High Temperature muffle furnace will be used. The figure 3.2 shows the furnace used for the co-pyrolysis process. There were total 3 samples tested namely coconut shell, PPE and coconut shell + PPE at 3 different sessions. 10 grams of each sample were placed in crucibles with high heat resistance to support the pyrolysis reaction in the vacuum chamber. The PPE and CCS were mixed at 1:1 ratio for co-pyrolysis process. The nitrogen cylinder was

connected to the furnace to sweep the gas internally to the condensing chamber. The flow was adjusted to 7 cc/min and allowed it to continue to do so until the experiment ends. The figure 3.4 shows the nitrogen gas tank used connected to the flow controller to control the nitrogen gas flow. The temperature was measured using an external probe due to inaccuracy of internal temperature gauge.



**Figure 3.2: Pyrolysis Furnace**



**Figure 3.3: The nitrogen gas flow adjusted at 7 cc/min**





**Figure 3.5: Crucible**



**Figure 3.4: Nitrogen Gas Tank**



**Figure 3.6: Temperature Probe**

The setting on the furnace was set in 3 stages. First to preheat the furnace to 550 °C, followed by retention time of 30 minutes and then cooled to room temperature at 27 °C. However, the pyrolysis process intended for this experiment is fast pyrolysis which require for the feedstocks to be subjected to high temperature immediately at around 550 °C. For this reason, the furnace was modified to fit an adjustable lever which will function to push the sample from the outside the chamber towards the middle after 1 hour of preheating, at the temperature of 550 °C.

As the maximum temperature for this pyrolysis set at 550 °C for this experiment, CW-5000 is adequate for the cooling process as indicated in figure 3.7 below. The cooling tubes were connected to the chiller to cool the volatile gas. The cooling setup consists of two stages of cooling with each connecting the condensing tube to the collecting flask. The flasks were submerged partially in the ice bath and replaced with new ice for each run. The end of this cooling setup was connected to the venting chamber to remove the remaining gas.



**Figure 3.7: CW-5000 Chiller**

Each pyrolysis process will take about 4-5 hours to complete. As we lack the facility for fast pyrolysis, the initial setup took time due to trial and error. The significant time spent for this experiment allowed us to obtain only three runs in total, each sample per

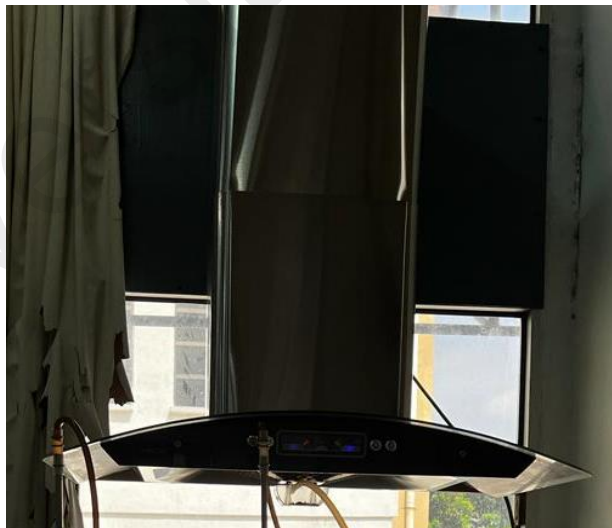
run. The setup can be illustrated as figure 3.11 below, note that the lever adjustment and chiller are not included for ease of illustration.



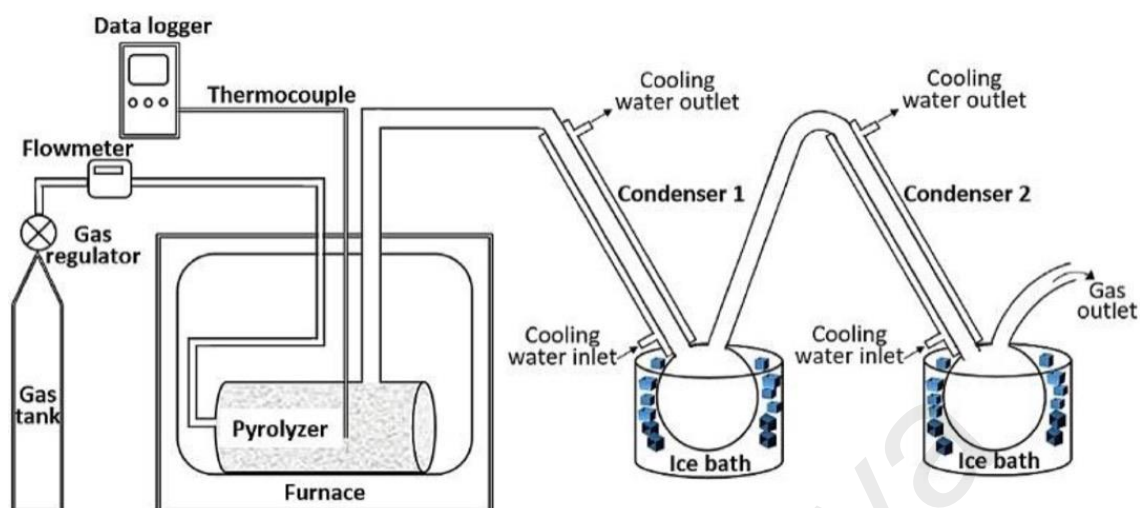
**Figure 3.8: Condensing Cylinder**



**Figure 3.9: Ice bath to cool the gas**



**Figure 3.10: Exhaust Chamber**



**Figure 3.11: Pyrolysis and Co-pyrolysis Setup (Azeta, O.Ayeni, Agboola, & B.Elehinafe, 2021)**

There were three products obtained namely coconut shell oil, PPE oil and finally the co-pyrolysis oil. The product obtained can be divided into three sub-categories which are gas, biochar and bio-oil. Each product are measured to calculate the weightage of the phases. This will give the idea of yield of phases respective to products. These oils were then sent for gas chromatography mass spectrometry analysis to study the components of the products. These product samples were also submitted to designated lab to conduct the TGA and DSC process.

In summary, the experiment procedure can be broken down as below. The first being the sample preparation followed by the setup preparation. Each time the experiment is run, the setup had to be cleaned thoroughly for the next run to avoid any contamination. After that, for each run, the sample is placed in the crucible and then into the furnace chamber. The lid gaskets of both ends had to sealed tightly to avoid any gas from escaping. The nitrogen gas was then allowed to flow and the furnace will be turned on for the run to begin. The pyrolysis was allowed to happen while maintaining the condensing tubes

and ice bath surrounding the collecting flask at low temperature. When the run is complete, the chamber had to be allowed to cool down for about two hours before able to collect the char from the chamber. The weight percentage is then calculated when the char and the condensed bio-oil measured. Any remaining oil droplets attached to the chamber's surrounding are wiped with paper towel and measured together to get the best sense of the total weight of oil accumulation. The char was stored in plastic bag while the oil collected placed in air-tight bottle and stored in incubator to avoid and heat contamination. The heating value was also measured for each sample.

For DCS and TGA, the dry samples are prepared. There were coconut shell powder, PPE cuts and mixed coconut shell powder with PPE cuts. After preparing the samples were sent for the lab analysis. The bio-oil obtained were also prepared and sent for GC-MS analysis.

## CHAPTER 4: RESULTS AND DISCUSSION

### 4.1 Sample weightage analysis

There were total of three oil samples analyses for this experiment namely, CCS oil, PPE oil and CCS + PPE oil. When the experiment was done their end products were collected and measured. However, due to tendency of oil sticking to the surface of the chamber, there will be some discrepancy that will occur. The following tables show the results obtained in terms of weight of phases and yield percentage when 10g of each oil sample subjected to the pyrolysis process.

**Table 4.1: Weight distribution of each product**

	PPE (g)	CCS (g)	CCS + PPE (g)
Biochar	5.07	5.15	2.86
Bio-oil	4.20	3.80	3.66
Gas	0.73	1.05	3.48

The weight percentage was calculated using the formula:

$$\text{Yield weight percentage (\%)} = \frac{\text{weight of phase}}{10\text{g (sample size)}} \times 100\%$$

**Table 4.2: Weight percentage distribution of each phase**

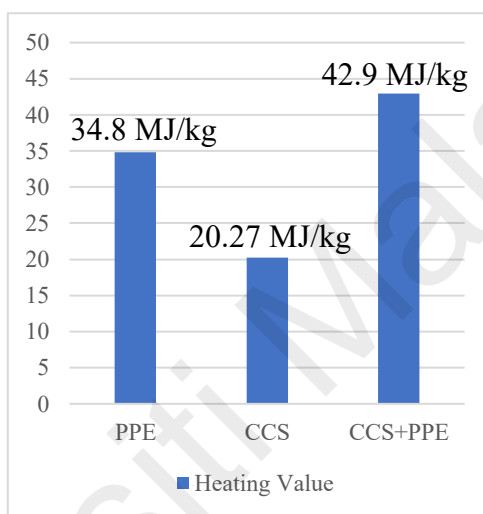
	PPE (%)	CCS (%)	CCS + PPE (%)
Biochar	50.7	51.5	28.6
Bio-oil	42.0	38.0	36.6
Gas	7.3	10.5	34.8



The proximate and ultimate analysis and heating value for PPE, CCS and CCS + PPE can be referred to table below.

**Table 4.3: Proximate and ultimate analysis of PPE, CCS and CCS+PPE**

Type of Material	Proximate Analysis (wt %)				Ultimate Analysis (wt %)			
	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	N	O
PPE	0.00	89.45	4.79	5.76	77.41	14.78	7.7	0.11
CCS	7.98	76.01	19.1	1.96	53.31	6.93	0.87	38.62
CCS+PPE	-	-	-	-	-	-	-	-



**Figure 4.1: Heating value of each sample product**

From the table 4.2, it can be observed PPE produced the highest amount of bio-oil. However, it also been observed there was accumulation of wax in the collection flask which contributed to the overall weight of the bio-oil. It also released the least amount of gas as due to high amount of volatile matter indicated in the proximate analysis in table 4.3, most of the gas was converted into the oil. This fact agrees with (Kumar & Singh, 2011) where the author found the higher the volatile compounds in the feedstocks, the higher the oil yield. However, the author also mentioned there was formation of wax which is similar to this experiment. The char produced in the PPE mostly due to the



carbon content. This could be due to the Polypropylene plastic during the production of PPE derived from petroleum product like hydrocarbon. It was also observed, there was no moisture present in the PPE which can be due to absence of organic components such as lignin or cellulose which are prominent components in the biomass. The high hydrogen component as mentioned in the previous literature such as (Abbas-Abadi, Van Geem, Hossein Bazgir, & Ghadiri, 2021), was also found in the composition of PPE and this will be acting as the donor for co-pyrolysis process that will be explained further in this paper.

Moving on to the CCS, there was high amount of char produced which is as expected from an organic material. This is mainly due to the high fixed carbon content that converts the feedstocks during pyrolysis into char. Comparing with PPE, CCS has lesser volatile matter and this can be translated into the lower volume of bio-oil obtained. However, comparing with other feedstocks mentioned in the previous studies in literature review, CCS does still give very good yield of oil. The higher fixed carbon also explains the lower amount bio-oil yield at 38%. Notice that biomass, due to not being derived from hydrocarbon, the hydrogen and carbon content is much less than PPE. Furthermore, as mentioned by (Balasundram, et al., 2017), to yield high amount of bio-oil, O/C ratio of the feedstocks must be high and this experiment agrees with the author's statement as these two components were found abundant in the CCS and thus yielded high amount of oil comparatively. Due to units related to the oxygen, the bonds are easily broken down to form volatile matter. Besides, like most of the biomass, the high oxygen content is inevitable. This combined with moisture presence in the CCS will affect the quality of the product. As seen in the figure 4.1, the heating values of each oil was measured and found CCS to exhibit the lowest amount at 20.27 MJ/kg. This is true to the statement mentioned before where high amount of oxygen and moisture presence will inhibit the heating value of the bio-oil. Thus, removal of oxygen is vital to improve the quality of

the oil in terms of heating value. This role will be carried out by the co-pyrolysis process as will be discussed below.

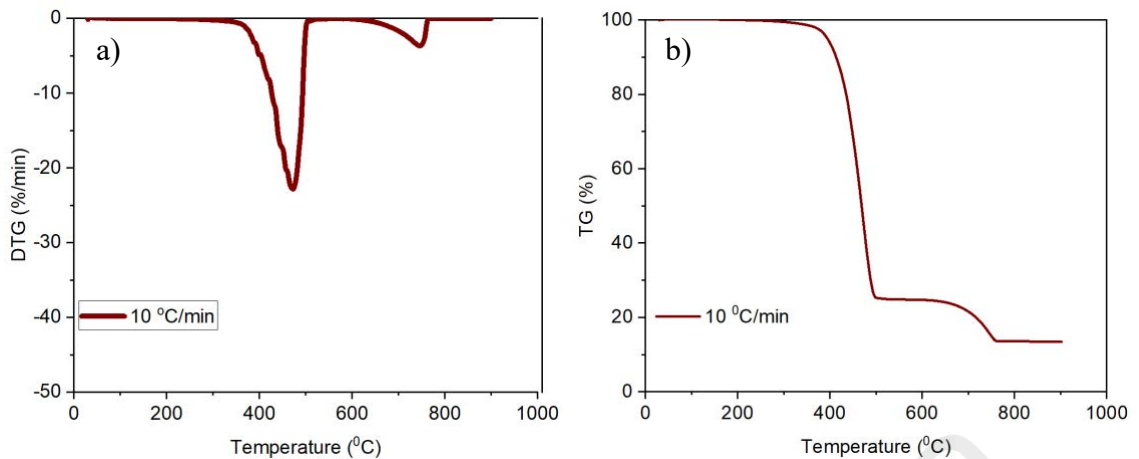
As the upgradation process for bio-oil, the co-pyrolysis was introduced into this experiment. From the table 4.2 above, it can be seen the percentage of the biochar reduced drastically about 43.6% from 50.7% to 28.1% when compared with PPE and about 44% reduction when comparing with CCS. This is also in agreement with the study conducted by (Abbas-Abadi, Van Geem, Hossein Bazgir, & Ghadiri, 2021) where the author find reduction in biochar during co-pyrolysis of plastics and oak. Furthermore, as the main goal of this experiment, the bio-oil yield decreased about 12.9% compared to PPE and 3.7% when compared to CCS. This is in actual disagreement (Hassan, Lim, & Hameed, 2019) where the author found there was 55% increase in bio-oil yield during co-pyrolysis of biomass and plastics compared to individual pyrolysis. Note that the oil reduction in PPE is much more prominent than the CCS. This is mainly due to high volatile content in the PPE compared to CCS and during co-pyrolysis the volatile matter in PPE reacted with CCS to form more of gas content. This can be seen in the table 4.2 where there is high increase in gas content for CCS+PPE about 79% when compared to PPE and 70% when comparing with CCS. Naturally, the high increase in volatile matter can contribute to increase in both gas and oil in the end product but during this specific experiment it only affected in increase in gas. The reason this happened can be theorized due to lack of cooling from the setup itself. When the pyrolysis gas passes through the condensing cylinder, it must be cooled sufficiently to form enough oil. This can be resolved by introducing dry ice during the water bath at the collecting flask to further reduce the temperature thus condensing in a better fashion. Another reason would be the condensed early in the chamber itself where the oil droplets attaches itself to the surface of the chamber. This phenomenon was observed during this experiment and the paper towel was

used to scoop the remaining oil for weighing. Though by this way some oil droplets cannot be completely extracted. Besides, the heating value tells another story completely. There is 23% increase in heating value in CCS+PPE at 42.9 MJ/kg compared to PPE at 34.83 MJ/kg and about 110% when compared to CCS at 20.27 MJ/kg. The sharp increase in heating value compared to CCS can be explained into two reasons. The first one is the reduction in moisture content when the CCS and PPE were subjected to co-pyrolysis. This statement is agreed by studies conducted by (Hassan, Lim, & Hameed, 2019) and (Shahdan, Balasundram, Ibrahim, & Isha, 2022). Another one is the reduction in oxygen content due to synergistic effect. The hydrogen from PPE acted as the hydrogen donor and reduced the oxygen content in the CCS forming a better-quality oil. As mentioned by (Kartik, et al., 2022), this might be also due to increase in carbon and hydrogen content emulating hydrocarbon. After all the purpose of producing bio-oil is to emulate hydrocarbon as mentioned by (Shahdan, Balasundram, Ibrahim, & Isha, 2022) which has range of 45 MJ/kg to 47 MJ/kg that will be able to be used as transport fuel.

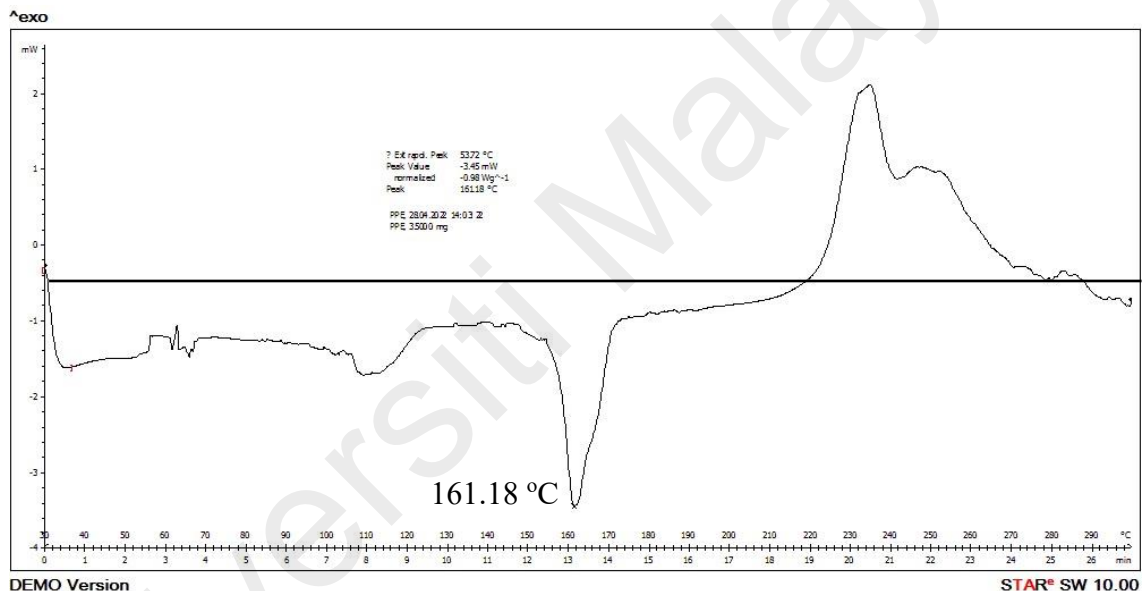
#### **4.2 TG and DSC analysis**

TG and DSC analysis were conducted on each sample to analyse the decomposition profile and the endothermic and exothermic events of the samples. The samples were subjected to heating from 30 °C to 900 °C at the rate of 10 °C/min at inert environment for TG. Any temperatures above or below the range would be deemed redundant as the current range was enough to provide usable trend. The DSC was also measured at however lower temperature range of 30 °C to 300 °C, which is enough to give good idea of the trend.

### PPE Analysis



**Figure 4.2: DTG (a) and TG(b) curves of PPE at heating rate of 10 °C/min**



**Figure 4.3: DSC curve for PPE at heating rate of 10 °C /min**

As seen in the plots above there were two plots obtained from the TG analysis which are derivative plot and the weight loss plot. While accurate analysis of the plots requires significant knowledge on translating, other literatures can also act as a guide to determine the trend on the plot itself. (Chen, Zhang, Xu, & Yuan, 2021) mentioned in their paper comparing different types of decomposition temperature range and activation energy value of many different feedstocks. The author mentioned medical waste like medical surgical mask rope should have decomposition range of 226-526 °C and polypropylene

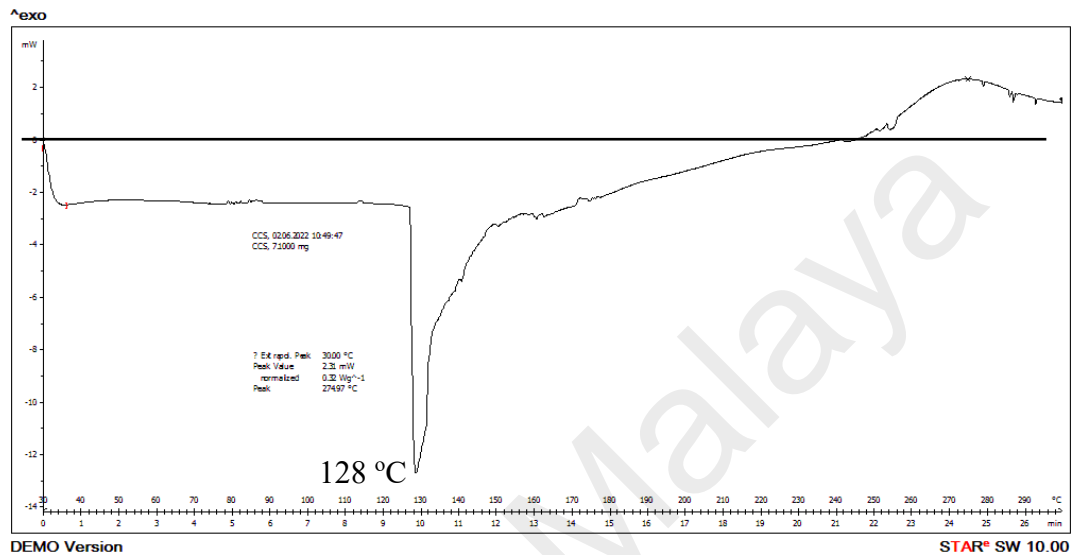
wastes should be in the range of 379-500 °C. Since there is a significant weight loss at temperature of 450 °C based on TG plot, it can be assumed the author was accurate to demonstrate the range. The significant temperature loss can be associated with high content of volatiles in PPE (Jiang, et al., 2021). At this stage of decomposition (Chen, Zhang, Xu, & Yuan, 2021) found the activation energy could be within the range of 153-265 kJ/mol. However, there is also a small curve occurred after the decomposition from temperature range of 450-750 °C. Based on the studies by (Chen, Zhang, Xu, & Yuan, 2021) this could be the indication of presence of phenolic FRP. However, it could also be indicated by the further decomposition of the char presence after all the volatile matter had been evaporated from the sample.

The DSC from the figure 4.3 shows the exothermic and endothermic process of the process. When the curve extends beyond 0 mW it is exothermic while below considered endothermic process. As indicated by the plot, the PPE sample underwent endothermic process from the beginning indicating energy absorbance. There is significant heat energy absorbance at 152-174 °C forming a peak at 161.18 °C. This indicates PPE reacts to heat at an early stage and probably due to medical PPE are not heat resistant and reacts quickly when subjected to one. The endothermic process was then followed by exothermic process where it happens from 225-268 °C. At this stage the PPE is beginning to change from its original matter into char while releasing volatile gas to the surrounding. Due to the gas's property of being flammable, it releases energy to the surrounding indicating exothermic process. After 268 °C, the temperature declines again which is when as indicated by the TG plot the PPE sample beginning to lose its weight.

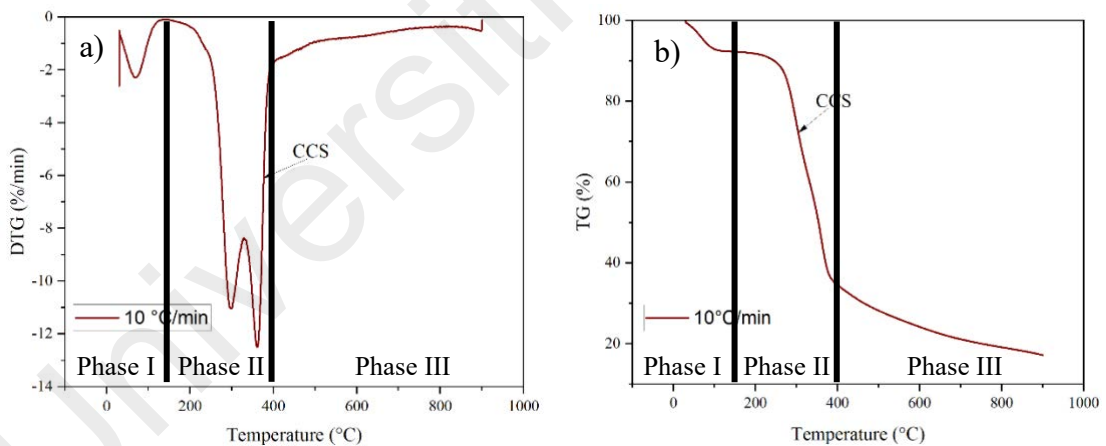
This analysis shows PPE does have volatiles that reacts to heat at an early stage and can be a good catalyst for the co-pyrolysis process. As mentioned above this might be

due to medical PPE not being flame resistant and react to heat easily compared to other types of plastic wastes. The reactivity and volatility of PPE is important for the synergistic effect during co-pyrolysis which will be explained later.

### CCS Analysis



**Figure 4.4: DSC curve for CCS at heating rate of 10 °C /min**



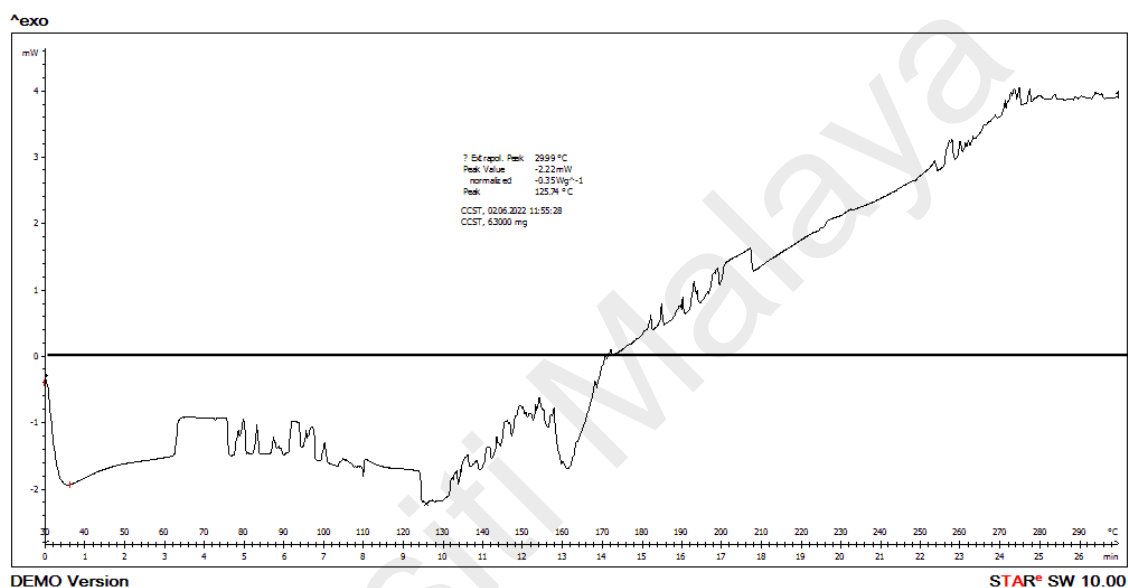
**Figure 4.5: DTG (a) and TG(b) curves of CCS at heating rate of 10 °C/min**

The mass loss curves of DTG and TG of biomass typically consists of three main phases of thermal degradation which are vaporization of moisture and light component, devolatilization of hemicellulose and cellulose and finally the lignin decomposition (Balasundram, et al., 2017). The vaporization of moisture for CCS happened at temperature below 170 °C as indicated by the figure 4.5 (a). At temperature range of 175-

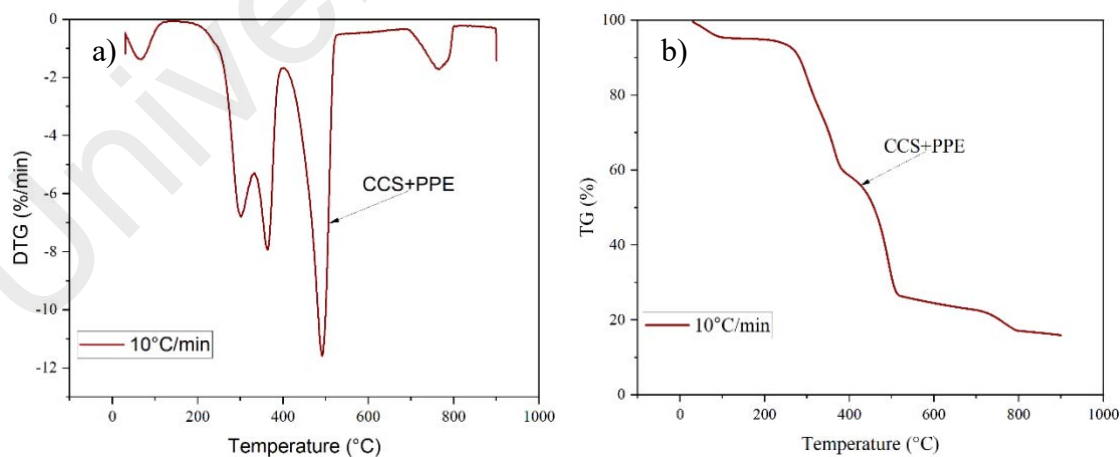
400 °C the phase has huge drop in weight percentage where the devolatilization of hemicellulose and cellulose happened. Beyond 400 °C till 900 °C, degradation of CCS occurs. The mass loss for CCS during first phase is at 6% which is the moisture content considered very low and it can greatly benefit in producing higher oil yield. This statement agrees with (Balasundram, et al., 2017) where the author mention to be good biomass feedstock it has to be below 10% moisture. The moisture must be reduced in order for heat propagation into biomass to happen to produce high amount of volatiles. As hemicellulose and cellulose are the major components of lignocellulosic in any type of biomass, a significant amount of temperature is required to breakdown the complex components into volatile products. This can be indicated in figure 4.5 (b) the major drop in weight percentage only occurs during second phase. Furthermore, at phase II in the figure 4.5 (a), there are two peaks can be seen. This phenomenon is discussed in the study conducted by (Collard & Blin, 2014) where the degradation of cellulose happens at the range of 330-370 °C and hemicellulose in between 200-350 °C. So, it can be explained that the first peak indicates the degradation of hemicellulose while the second one is the degradation of cellulose. Comparing with the findings of (Balasundram, et al., 2017), the author suggested if the catalysts was used during pyrolysis, the two peaks will merge into to one due to faster rate of degradation of cellulose and hemicellulose. The faster rate of degradation also helps to create higher amount of bio-oil during the pyrolysis process. When CCS is compared to PPE it can be seen the trend in CCS degradation happens at earlier temperature. Further evidence can be also seen in the DSC curve in figure 4.4 where in the CCS the heat is absorbed at 128 °C, a much lower temperature than PPE at 161.18 °C. However, CCS degradation happens at much lower rate when compared to PPE as shown by DTG figures 4.2 (a) and 4.5 (a). This indicates PPE is much more volatile than CCS and can function as a replacement for catalysts to lower the degradation

rate of CCS. The DSC figures also shows the difference in the height of exothermic peaks between the CCS and PPE. The PPE has much higher peak than CCS which further explains its higher volatility compared to CCS where the higher amount volatile gas is released to the surrounding which gives of high amount of heat energy. At phase III, it can be characterised as carbonization where the final residue will be formed.

### CCS + PPE Analysis



**Figure 4.7: DSC curve for CCS + PPE at heating rate of 10 °C /min**



**Figure 4.6: DTG (a) and TG(b) curves of CCS+PPE at heating rate of 10 °C/min**



From the figure 4.7 (a) it can be seen emulating similar stages to the DTG of CCS. However, there is a main difference where the first two peaks (250-400 °C) are actually the pyrolysis of the CCS which its components of hemicellulose and cellulose are being broken down. The peaks can also be observed much shorter when compared to actual pyrolysis of CCS. This shows the CCS is broken down much slower when mixed with PPE. Similarly, the third peak which is the PPE can also be seen reduced in its peak height significantly when mixed with CCS compared to just individual pyrolysis of PPE. This may indicate the slower degradation and loss in weight due to the synergistic effect between the CCS and PPE. The trend can be also explained through the TG curve in the figure 4.7 (b) where the drop in weight percentage is much steadier and slower compared to both PPE and CCS. As the curve indicates, the drop in mass when PPE pyrolysis stage is higher at 35% compared to CCS at 30%. This might suggest the PPE had undergone the hydrogen donation to the oxygen rich compound CCS. Although addition of PPE to CCS should increase the degradation rate, the synergistic effect created a steadier degradation leading to higher amount of volatiles released as gas. This phenomenon is supported by the DSC curve in figure 4.6 where energy absorption happens only till 160 °C but energy is released continuously afterwards suggesting exothermic process. As more gas is released, the heat energy also increases as the trend shown in the DSC curve. One of the main goals of this study was to increase the yield of bio-oil produced through the synergistic effect. The trend shown may have indicated otherwise showing more volatiles released as gas. These gas however can be condensed further by cooling to yield more bio-oil that is much more volatile and reactive. This trend also explains why the weight percentage of the oil for PPE+CCS was lower as discussed earlier in this chapter. There might be better prospects if catalysts or different ratio were used to study further

the co-pyrolysis between CCS and PPE but due to time constraints it was not possible to do so.

### 4.3 GC-MS Analysis

**Table 4.4: GC-MS of PPE Bio-oil**

Height (%)	Compounds	Height (%)	Compounds
5.38	Toluene	4.39	Dotriacontylpentafluoropropionate
4.6	Isobutylacetate	0.73	Tetracosyltrifluoroacetate
4.38	2-Pentanone,4-hydroxy-4-methyl-	0.44	Octatriacontyltrifluoroacetate
2.92	Ethylbenzene	3.02	1-Decanol,2-hexyl-
1.78	o-Xylene	0.73	Docosylheptafluorobutyrate
0.64	o-Xylene	0.64	9-Octadecen-1-ol,(Z)-
0.75	Isodecylmethacrylate	2.91	1-Nonadecene
0.53	(2,4,6-Trimethylcyclohexyl)methanol	1.46	1-Decanol,2-hexyl-
0.72	1-Tridecene	4.05	1,22-Docosanediol
0.59	Dodecane	1.21	Heptasiloxane,hexadecamethyl-
0.72	1-Tridecene	0.74	1,22-Docosanediol
0.55	Tridecane	0.56	Octatriacontylpentafluoropropionate
3.56	11-Methyldodecanol	0.98	Oxirane,hexadecyl-
1.13	2-Isopropyl-5-methyl-1-heptanol	2.36	1-Nonadecene
2.8	2-Isopropyl-5-methyl-1-heptanol	1.15	Eicosane
0.47	1-Octacosanol,2,4,6,8-tetramethyl-,	1.25	10-Dodecen-1-ol,7,11-dimethyl-
1.12	Cyclododecanemethanol	0.75	Cyclohexane,1-ethyl-2-propyl-
1.62	1-Tetradecanol	4.39	Nonadecylpentafluoropropionate
1.13	Tetradecane	1.41	Docosanoicacid,
0.42	Naphthalene,2,6-dimethyl-	0.76	9-Octadecen-1-ol,(Z)-
0.4	11-Methyldodecanol	2.37	1-Nonadecene
1.61	n-Pentadecanol	1.2	Eicosane
1.45	3-Butoxy-1,1,1,7,7,7-hexamethyl-3,5,5-tris(trimethylsiloxy)tetrasiloxane	3.9	Cyclohexane,1,2,3,5-tetraisopropyl-
1.25	Phenol,2,4-bis(1,1-dimethylethyl)-	2.72	Bicyclo[2.2.1]heptane-2,5-dione,1,7,7-trimethyl-
2.6	1-Hexadecanesulfonylchloride	1.22	Hexadecane
0.81	1-Hexadecanesulfonylchloride	0.56	1-Decanol,2-hexyl-
1.3	1-Decanol,2-hexyl-	1.3	Cyclooctasiloxane,hexadecamethyl-
0.51	Heneicosylheptafluorobutyrate	0.62	9-Octadecen-1-ol,(Z)-
2.64	1-Nonadecene	2.03	1-Nonadecene
0.92	10-Dodecen-1-ol,7,11-dimethyl-	0.85	Eicosane

GC-MS analysis was conducted on all three samples bio-oil products from their respective pyrolysis including PPE, CCS and CCS+PPE. The table 4.4 indicates the degradation compounds of PPE or SMS that is entirely made out of polypropylene. So, most of the components should have vast similarities to the degradation of PP. As listed in the table, pyrolysis of PPE produces oxygenated compounds (alcohols, ketones phenols, etc.) and hydrocarbons such as aromatics (Toluene, 2,6-dimethyl-Napthalene and O-xylene) and aliphatic (1-Nonadecene, Tridecane, Dodecane etc.). However, the percentage of hydrocarbon or the carbon-based compounds are much more prominent in the PPE. The oxygenated compounds found less in percentage in PPE product as typically these compounds are found in the pyrolysis product of biomass. The produced hydrocarbons from PPE are also volatile in nature. The compounds produce also high in C/H ratio as explained by (Wang, et al., 2022) and (Balasundram, et al., 2017) which contributes to better oil yield. The authors also mentioned have high O/C will eventually lead to high production of gaseous state rather than in liquid state.

**Table 4.5: GC-MS of CCS Bio-oil**

Height (%)	Compounds	Height (%)	Compounds
19.69	Toluene	1.67	1-Pentadecene
16.31	Isobutylacetate	2.96	Tetradecane
1.32	3-Penten-2-one, 4-methyl-	0.97	Naphthalene,2,6-dimethyl-
15.1	2-Pentanone, 4-hydroxy-4-methyl-	1.38	Naphthalene,2,6-dimethyl-
9.89	Ethylbenzene	1.29	Hexadecane
6.03	o-Xylene	2.97	Phenol,2,4-bis(1,1-dimethylethyl)-
2.1	o-Xylene	3.09	1-Nonadecene
4.02	Phenol	1.82	Hexadecane
0.79	Cyanicacid, ester	2.67	1-Nonadecene
1.31	Dodecane	0.85	Eicosane
1.18	Tridecane	0.49	Nonyl-2,3-didesoxy-.alpha.-D-erythrohex-2-enopyranoside
0.52	Naphthalene,2-methyl-	1.57	1-Nonadecene

Unlike PPE pyrolysis, the CCS bio-oil was made up of much less compounds and can be mostly associated to the oxygenated compounds. Like most of the bio-oil CCS does share the presence of aromatic hydrocarbons however due to high presence of O/C ratio compounds in CCS, high amount of oxygenated compounds can also be detected. This can be seen from the presence of phenols and esters that has high amount of O/C ratio compounds. Although it has higher O/C compounds compared to PPE, it is still much better in terms of biomass feedstock when compared to other biomass. In a study conducted by (Jiang, et al., 2021) where pyrolysis of *Chlorella vulgaris*, a type of micro algae produces much higher amount of oxygenated compounds such as furfural, phenols acids and even ketones. Comparatively, CCS produced more hydrocarbon-based compounds which is preferable in this case. One might also argue, due to this, the reaction with PPE will be much less efficient compared to the micro algae because hydrogen deficient compounds in biomass has better synergistic effect to create higher amount of bio-oil.

**Table 4.6: GC-MS of PPE+CCS Bio-oil**

Height (%)	Compounds	Height (%)	Compounds
17.79	Toluene	0.86	Phenol,2,6-dimethoxy-
15.45	Isobutylacetate	1.53	1-Tetradecanol
1.17	3-Penten-2-one,4-methyl-	2.71	Tetradecane
14.63	2-Pentanone,4-hydroxy-4-methyl-	0.93	Naphthalene,1,8-dimethyl-
9.43	Ethylbenzene	1.36	Naphthalene,1,8-dimethyl-
5.5	o-Xylene	1.21	Heptadecane
1.93	o-Xylene	2.03	Phenol,2,4-bis(1,1-dimethylethyl)-
11.49	Phenol	2.66	1-Nonadecene
0.82	Silanediol,dimethyl-,diacetate	1.61	Hexadecane
1.21	Dodecane	2.9	1-Nonadecene
1.2	Naphthalene,2-methyl-	1.59	1-Nonadecene

When co-pyrolysis is introduced between PPE and CCS, there were significant difference in compounds produced in the bio-oil. The amount aromatic hydrocarbons such as toluene, ethylbenzene, o-xylene, etc. had huge improvement when comparing with PPE. This is as explained before, the oxygenates from the CCS had synergistic effect with PPE which acted as the hydrogen donor in this case. Some compounds from co-pyrolysis when compared with CCS though had reduced marginally especially the hydrocarbon units. Although, it may seem like a disadvantage here, during the co-pyrolysis the PPE successfully removed several heating value inhibiting oxygenates. In previous section, it has been discussed about CCS having less oxygenates compared to other biomass. While the oxygenates had been removed, the CCS introduction created a high hydrocarbon ratio oil while also creating more volatiles when synergised with PPE in gaseous state. This is why it was observed in the weight percentage analysis, there were marginally lesser amount of bio-oil collected compared to pure PPE and CCS. However, through observation, the oil was also less viscous and this can be attributed to its high heating value leading to a better quality of oil.

## CHAPTER 5: CONCLUSION AND RECOMMENDATION

### *Conclusion*

There are several conclusions that can be derived from this study. Firstly, the decomposition of each pyrolysis indicates, as TG curves indicated, PPE decomposes at temperature around 400 °C, CCS at around 200 °C and CCS+PPE at 220 °C. This indicates addition of CCS to PPE had greatly reduced the decomposition temperature from 400 °C all the way to 220 °C. This is due to the synergistic effect between the two where CCS being hydrogen deficient and oxygen rich component able to receive hydrogen components from the PPE to form hydrocarbon. This also resulted in much lesser amount of char produced in the co-pyrolysis process when compared to the pure ones. Lowering the decomposition temperature also enabled a longer and steadier decomposition rate where more volatiles had been released. However, this also resulted in more of the product formed in gaseous state making the oil yield lesser than the pure pyrolysis. This phenomenon as explained before likely due to the already presence of high hydrocarbon compounds in the CCS itself. On the other hand, through weight percentage analysis, addition of hydrocarbon compounds did increase the heating value by 20% at 42.9 MJ/kg when compared to PPE at 34.8 MJ/kg and a massive 50% when compared to CCS at 20.27 MJ/kg. From this observation, although the produced bio-oil amount is less, the quality in terms of heating value had greatly increased indicating the increase in quality of the final product.

### *Recommendations*

However, there are still several recommendations that can be made based on this study to further understand and improve the final product. Due to time constraints, the ratio used for this study is 1:1 of PPE to CCS. Many studies had shown ratio can be a great variable to produce different outcomes. As such in this case, the ratio of PPE should be increased to produce higher yield. The high volatile nature of PPE can be counteracted by using more of it during the co-pyrolysis to yield more bio-oil. Another factor is the temperature of the pyrolysis process. Through the literature review, the PP in PPE has better prospect of yielding more oil when subject to lower temperature. While this study had been done at 550 °C which is not far from the recommended 500 °C, lowering the temperature might improve the oil yield. This study was also conducted in a DIY fast pyrolysis furnace as the lever is used to time the sliding of the sample to the middle of the chamber. By using a proper fast pyrolysis furnace, there is a possibility of high oil yield.

This study has shown there is a way to treat both PPE and CCS in a much greener way. Both of these feedstocks can be largely found in Malaysia and other countries. Co-pyrolysis of both of these had been proven beneficial in creating hydrocarbon that mimics the petroleum-based hydrocarbon. As such, further study into this subject is recommended since it has the potential for a high-quality hydrocarbon product.

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