INVESTIGATIONS INTO THE UTILISATION OF CHICKEN LITTER FOR POWER GENERATION

A thesis submitted for the degree of Doctor of Philosophy

by

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ABSTRACT

Chicken litter is commonly used as bio fertilizer or soil ameliorant due to its high content of nutritional components such as nitrogen (N), phosphorus (P) and potassium (K). Oversupply of chicken litter to land, however, may cause problems due to the built-up of excessive nitrogen which oxidises, forming nitrates and ammonia compounds. The highly concentrated nitrates can contaminate both surface water and groundwater, which are sources of drinking water. Evaporation of ammonia also causes odour problems in the surrounding areas. With fast increasing chicken production, and limits on the use of chicken litter as fertilizer on local farms an alternative utilisation approach is the use of chicken litter for energy production. Energy production from chicken litter is of particular interest in developing countries where electricity supply from the grid may not be existent or is highly unreliable.

Possible technologies for the conversion of chicken litter to energy are *combustion*, *anaerobic digestion*, *gasification* and *pyrolysis*. Literature review of these methods has indicated that considering energy conversion efficiency, economic and environmental factors, pyrolysis can be a suitable method for application in developing countries such as Indonesia. For this reason, this thesis focuses on pyrolysis and its potential to produce char, syngas and bio oil yield.

Three types of pyrolysis have been studied. These include: slow pyrolysis in the temperature range 350°C - 450°C, intermediate pyrolysis at the temperature range 500°C -700°C and fast pyrolysis in the temperature range 400°C – 600°C. The types of chicken litter used as the feedstock in slow pyrolysis were hay mix (chicken manure + hay), straw mix (chicken manure + straw), rice husk mix (chicken manure + rice husk), wood shavings mix (chicken manure + wood shavings). For the intermediate pyrolysis, fresh chicken litter (FCL) from Ireland and pelletized chicken litter (PCL) from Finland were used. For the fast pyrolysis experiments, only PCL was used.

The result of the chicken litter pyrolysis experiments showed that the dominant product was char in the slow pyrolysis, liquid (bio-oil) in the intermediate pyrolysis and gas (syngas) in the fast pyrolysis. In addition to the experiments, simulations were performed using Aspen plus, to determine the maximum amount of electric energy that can be generated from the pyrolysis of chicken litter. The simulations were based on chicken litter from a farm with a production of 400,000 birds/batch. Liquid yield was determined from the experiments to have the highest calorific value, and thus, the simulations were performed using the parameters and results from the experiment that generated the highest level of liquid yield-this was the FCL pyrolysis at temperature of 500 °C.

The simulation revealed that the heat from the combustion (burning) of all gas yield plus 35% of char yield would be sufficient to serve as the heat input for pyrolysis process. The heat from combustion of the liquid yield was then used as the energy input to an ORC system to generate electrical power. The results showed that the system with could produce electrical output of around 150 kW with an overall conversion efficiency of 6.5%. Economic analysis using the Net Present Value (NPV) methodology and investment conditions in Indonesia has shown that, assuming all the electrical energy generated and 65% of the char yield is sold, the system would produce a return on investment of 9 years. Improvements in ORC efficiency and reduction of capital cost as well as reduction in interest rates (currently 12% in Indonesia) is expected to lead to increased return on investment and improved viability of these systems for both energy security and reduction of environmental impacts in developing countries.

PUBLICATIONS

Title : **Investigation of chicken litter conversion into useful energy resources by using low temperature pyrolysis**
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NOMENCLATURE

C_i	Initial investment (IDR,€,£)
C_S	Specific ORC cost (€/kW)
$C_{S,ref}$	ORC specific cost reference (€/kW)
$f_{C_2H_4}$	ethylene fraction (vol%)
$f_{C_2H_6}$	ethane fraction (vol%)
f_{CH_4}	methane fraction (vol%)
f_{CO}	carbon monoxide fraction (vol%)
f_{H_2}	hydrogen fraction (vol%)
Fn	yearly cash flow (IDR,€,£)
$\bar{h}^o{}_{f,C_aH_bO_c}$	enthalpy of formation substance (kJ/mol)
$\bar{h}^o{}_{f,CO_2}$	enthalpy of formation CO_2 (kJ/mol)
$\bar{h}^o{}_{f,H_2O}$	enthalpy of formation H_2O (kJ/mol)
$\bar{h}^o{}_{f,O_2}$	enthalpy of formation O_2 (kJ/mol)
$h\mathrm{c}$	enthalpy of combustion (kJ/kg)
$h_{CHICKEN\ LITTER}$	energy specific from chicken litter (kJ/kg, kJ/mol)
h_{CHAR}	energy specific from char (char yield from pyrolysis process) (kJ/kg, kJ/mol)
h_{GAS}	energy specific from gas (gas yield from pyrolysis process) (kJ/kg, kJ/mol)
h_{TAR}	energy specific from tar (tar yield from pyrolysis process) (kJ/kg, kJ/mol)
K	discount rate (%)
n	time period (year)
N	years of investment’s life (year)
Q_h	Mass flow rate of dry feedstock (tonne/h)
Q_{Liq}	Liquid yield flow rate (tonne/h)
TPC_P	Total plant cost of pyrolysis reactor system (IDR,€,£)
TPC_S	Total plant cost of liquid storage system (IDR,€,£)
W_{net}	ORC capacity to be installed (kW)
$W_{net,ref}$	ORC capacity reference (kW)

ABREVIATION AND GLOSSARY

A	Ash content (wt%)
ar	as received basis
C_2H_2	acetylene
C_2H_4	ethylene
C_2H_6	ethane
CH_4	methane
CHP	combined and heat power
CO	carbon monoxide
CO_2	carbon dioxide
daf	dry ash free basis
db	dry basis
FC	Fix carbon content (wt%)
FCL	fresh chicken litter
GC MSD	gas chromatograph mass selective detector
H_2O	water
H_2S	hydrogen sulphide
HHV	higher heating value
K	potassium
LHV	lower heating value
MC	Moisture content (wt%)
Micro GC	micro gas chromatograph
NH_3	ammonia
O_2	oxygen
ORC	Organic Rankine cycle
P	phosphorus
PCL	pelletized chicken litter
TGA	thermogravimetric analysis
TGAr	thermogravimetric analyser
TIC	total ion current
VM	Volatile matter content (wt%)

vol%	volume percentage basis
wt%	weight percentage basis

Anaerobic digestion	a method of breaking down and converting a biomass into gas via a biological process in the absence of oxygen
Aspen Plus ^{TM}	simulation software based on mass and energy balance, and is made by unit blocks for reactors, heat exchangers, separators, pumps and compressors. The unit blocks are connected with the streamline, which represents the mass flow, heat flow or work.
Biochar/char	charcoal produced from biomass (plant)
Bio-oil/oil/tar	Bio crude oil
Chicken	type of domestic fowl
Chicken litter	blend of chicken manure, bedding material, spilled feed and water for animal, and some feathers
Chicken manure	faces of chicken
Combustion	the process of burning a material with the help of oxygen
Crucible	sample holder for proximate analysis
Feedstock	material to supply the experiment process
Fertilizer	chemical or natural substance added to soil or land to increase its fertility
Gasification	thermal decomposition process by heat in the presence of oxygen that transform biomass or organic materials into synthesis gas.
Hay mix	Mixture of 50% hay and 50% chicken manure (weight basis)
Inorganic	compounds that are not organic (not containing carbon)
NPV	net present value
Organic compounds	compounds derived from natural or living matter
Poultry	domestic fowl, such as chickens, turkeys, ducks, and geese
PP	payback period
Pyrolysis	thermal decomposition process by heat in the absence of oxygen. Bio-oil/oil/tar, gases and biochar/char are the product.

R1233ZD	Refrigerant code for CF3-CH=CCIH (Trans-1-chloro-3,3,3-trifluoropropene)
R245fa	Refrigerant code for $CF_3CH_2CHF_2$ (1,1,1,3,3-pentafluoropropane)
Rice husk mix	Mixture of 50% rice husk and 50% chicken manure
Soil ameliorant	substance that added to improve the soil quality.
Straw mix	Mixture of 50% straw and 50% chicken manure
Syngas	Synthesis gas
Wood shavings mix	Mixture of 50% wood shavings and 50% chicken manure

CHAPTER 1 INTRODUCTION

1.1 Background

Based on resource availability, energy can be categorised as renewable and non-renewable. Fossil fuel as an energy resource belongs to the category of non-renewable energy, which, up to present time, is still dominating as the most used energy resource in a large number of countries. Oxidation process or combustion is a conversion process that is often used for fossil fuel. This type of process results in carbon dioxide gas emissions that makes up the majority of emissions from the process. Along with other emission gases such as Nitrogen Oxides (NOx) and Sulphur Oxides (SOx), carbon dioxide will accumulate and form greenhouse gasses in the atmosphere. The United Nations' Food and Agriculture Organization (FAO) reported that 14.5% of the total greenhouse gases come from the farming sector, with chicken farming contributing 8% of this figure [1].

Climate change and the increasing temperature of the earth will continue as the greenhouse gases keep accumulating. It is of high importance, therefore, to take action to reduce the production of greenhouse gasses, in order to reduce global warming and its effects. Converting farming waste or litter to an alternative energy resource can make a contribution to this as well as improve the economic competitiveness of the farming industry itself. This chapter outlines the importance of energy generation from chicken litter and summarises the aims and objectives of this thesis.

1.2 Energy consumption

According to the international statistics bureau, the world heavily relies on fossil fuel. As shown in Figure 1.1, the use of fossil fuels reached 79.7% in 2017. On the contrary, the use of modern renewable energy was only 10.6%, the rest used nuclear energy, and the renewable energy consumption was decrease from 19.1% in 2013 to 18.1% in 2017. Another source of renewable energy that has been widely used is biomass. Biomass is biological material derived from living, or recently living organisms [2].

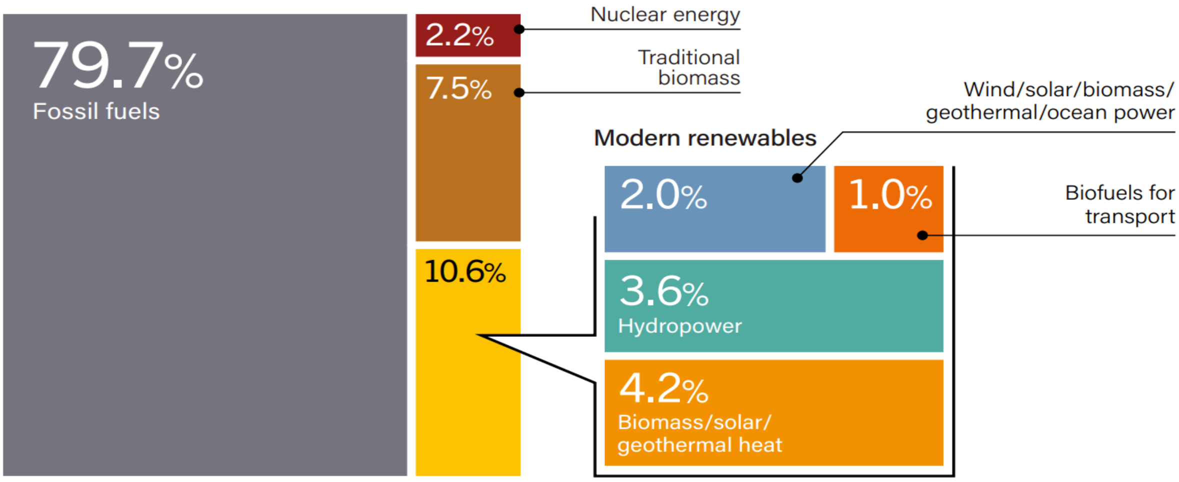


Figure 1. 1 Renewable Energy Share of Global Final Energy Consumption, 2017 [2].

Supporting the data from the international statistics bureau, energy outlook from British Petroleum (BP) reported that energy consumption from 2017 to 2040 is predicted to rise by 32%. Among the sources of energy used in 2017, fossil fuel is still the one that is dominantly used. Fossil fuels satisfy around 85% of the growth in energy demand and globally they are expected to account for almost 73% of total energy demand in 2040 (down from 85% in 2017). The use of renewable energy is also rising rapidly at 12.3% p.a. and their contribution is expected to rise from 4% presently to 15% by 2040 [3].

The increase in energy demand leads to increase in greenhouse gas emissions and accelerates climate change. To address this, the EU has revised the climate and energy framework, and committed to reduce greenhouse gas emissions by 40% compared to 1990 level, increasing the share of renewable energy to 32% of total EU energy consumption and make energy efficiency improvements of 32.5% for the period from 2021 to 2030 [4].

Compare to the chart from REN (figure 1.1), in Indonesia, as shown in Figure 1.2, even though fossil fuel consumption is more than 76%, the renewable energy supply can reached 24% of the total energy demand. The share of renewable energy consumption is dominating by the biomass section. From the total energy consumption, biomass consumption reaches 19%, whereas hydropower consumption is 3%, and biofuel (biodiesel and bioethanol) and geothermal is only 1% each of them [5].

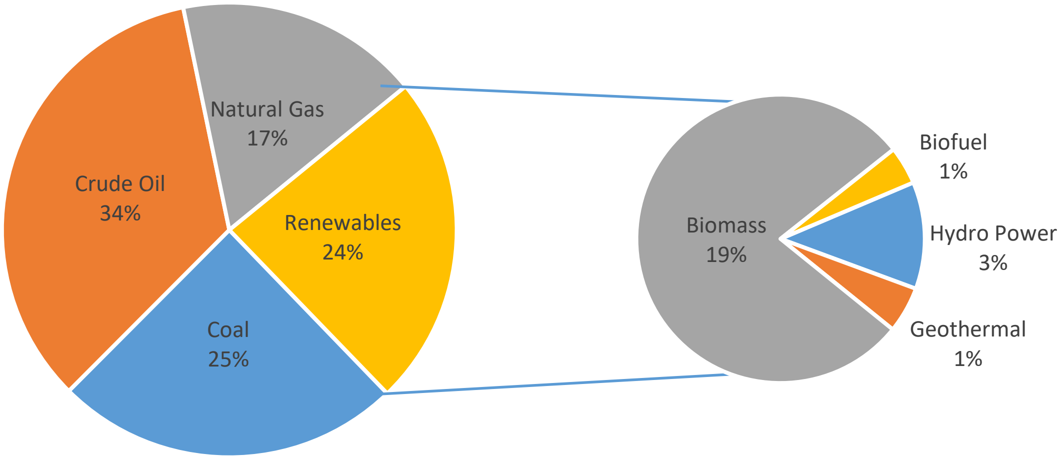


Figure 1. 2 Indonesian Primary Energy Supply by Sources, 2017 [5].

1.3 Biomass use

Biomass is categorised as a fuel derived from organic material and it includes firewood (woodened base material and the waste, and charcoal), agriculture waste, urban and industrial waste [5]. The largest source of biomass production in Indonesia comes from rice plant residue (husk, bran, stalk and straw), with the production that reaches up to 65.5 million tons per year [6]. In general, after harvesting time, the collected rice straws and stalks are dried and directly burned on the field or brought for the cattle feeding [7], [8]. Meanwhile, rice husks obtained from rice mills are collected. Using the method of combustion or direct burning, the dry or briquetting rice husks are burned and used as heat source in household stoves (Figure 1.3) [6], [9], [10].

Figure 1. 3 Rice husk utilisation, (left) stove using dry rice husk [11] and (right) rice husk briquette [12].

Besides the use as energy source, rice farm residue such as rice husks can also be used as bedding materials in animal farming. Some experiment had been done in order to examine the effect of using several type of bedding materials into the chicken farming production. By using several biomass types or agricultural waste, such as sawdust, sugarcane bagasse, straw and rice husk as bedding material for chicken farming, the experiments delivered a conclusion that there were statistically no adverse effect or alteration in quality of chicken farming production [13]–[15]. The farming production quality is including chicken weight gain, food consumption and liveability number [15].

In chicken farming, bedding materials will blend with chicken manure, spilled feed and water for animal, and some feathers become chicken litter. To maximize the animal health and productivity, beddings have to be renewed regularly. To add the economic value of chicken farming, use of bedding materials as well as chicken manure (chicken litter), which is rich in micro nutrients such as nitrogen (N), phosphorus (P) and potassium (K), can be utilized as natural fertilizer or soil amendments [16]–[18]. In addition, since the chicken litter contains biomass, surplus litter can be converted into useful energy resources. There are several methods that are widely used in biomass conversion, namely combustion, anaerobic digestion, pyrolysis and gasification [19]–[21]. The selection of conversion method for the present experiment is based on the highest caloric value, and it was found that the bio-oil yield product from pyrolysis of chicken litter has the highest caloric value, 28-29.6 MJ/kg [21], [22].

Pyrolysis is a heating or decomposition process with the working temperature between 300-700°C set within an environment with limited or no oxygen [23]. The pyrolysis of chicken litter generates three yield products namely bio-oil, synthesis gas and char. Each yield has different percentage of composition, depending on the type of pyrolysis process. In general, the process of pyrolysis is categorised into slow and fast pyrolysis. The dominant product of the slow pyrolysis process is char, while the process of fast pyrolysis generates more liquid and synthesis gas [19], [24], [25].

1.4 Research gap

According to the Organisation for Economic Co-operation and Development (OECD), the consumption of chicken in some countries, including Indonesia, rose significantly. In 2018, it was reported that chicken consumption in Indonesia was 7.06 kg/capita/year, which is one percent higher compared to the previous year [26]. As the demand for poultry meat increases, so does the production and waste.

If not treated accordingly, the chicken litter accumulation may bring a negative impact for the environment. Pathogens or harmful microorganism such as Escherichia Coli and Salmonella would easily grow and cause diseases [27]–[29]. Not only promoting the growth of bacteria, long-term accumulation of chicken litter may promote the formation of gases such as ammonia, nitrite, and sulphide gases that cause bad odour issues [29]–[31]. The conventional practice in Indonesia is to use chicken litter as fertilizer. When the demand for fertilizer in the farm or local area is met, the surplus is incinerated. Besides direct burning (combustion), as mentioned previously, there are several methods to convert chicken litter (as biomass) into useful resources, for example gasification and pyrolysis. Pyrolysis method is selected because the yield product generates the high caloric value content.

Presently, several modifications of reactor models as well as a variety of variables, such as temperature, residence time and additional materials, have been developed, aiming to maximize the result of pyrolysis process [32]. Pyrolysis plants that are using biomass as feedstock are available and are being continually developed in several countries [32]–[34]. Despite the rapid development of pyrolysis technology in some countries, chicken litter pyrolysis has not been developed at commercial scale [20]. This provides a reason to perform this study, which focuses on chicken litter pyrolysis and its application within the context of chicken farming conditions in Indonesia.

1.5 Research Aim and Objectives

Related to the research gap, the overall research aims to investigate ways to maximise the conversion of chicken litter into useful resources such as energy and biofertilizer. Specifically, the use of biomass may also help to overcome the negative effect of chicken litter that has been increasing due to the growing consumption of chicken meat.

The objectives of the research are to:

- Investigate the characteristics of chicken litter from different localities by its proximate and ultimate analysis, including the thermal decomposition by Thermogravimetric analysis (TGA).
- Consider advantages, disadvantages and economics of using different methods of conversion of chicken litter to useful resources, such as anaerobic digestion, combustion, gasification and pyrolysis.
- Select the most appropriate method of conversion of chicken litter to energy.
- Undertake detailed analysis of the selected method in terms of efficiency of conversion and resulting products of pyrolysis.
- Using process modelling determine the feasibility of the use of chicken litter for power generation in Indonesia.

1.6 Thesis structure

- **Chapter 1: Introduction**

  This chapter provides the background of the research related to the situation in Indonesia and the research gap identified from the methods of chicken litter conversion into useful resources. To address the research gap, the aim and objectives of the project were established.

- **Chapter 2: Literature Review**

  Chapter 2 provides a general review related with the research and the selection of the most appropriate technology for the conversion of chicken litter to energy and other resources.

- **Chapter 3: Materials and Methods**

  This chapter details the research methods used in the experimental investigations and the materials selected for the analysis. Four different chicken litter and bedding materials were selected to represent the characteristics in different areas of Europe and Indonesia.

- **Chapter 4: Pyrolysis Experiments**

  This chapter provides information on the pyrolysis conversion process and the design of a test system in the laboratory for slow pyrolysis tests based on information published in the literature.

- **Chapter 5: Data Analysis**

  Findings from the experiments and modelling investigations are discussed in this chapter. The analysis includes mass and energy balances for the chicken litter and bedding materials investigated, and energy conversion efficiencies for different power generation systems.

- **Chapter 6: Modelling and economic analysis**

  Aspen Plus^{TM} software was used to model the process of converting chicken litter including bedding materials through pyrolysis and energy production through the Organic Ranking Cycle (ORC) system.

- **Chapter 7: Conclusions and recommendations for further work.**

  This chapter summarises the main conclusions from the work and provides recommendations for further work in the area.

CHAPTER 2 Literature Review

2.1 Overview

The feedstock for the experiments was litter from chicken farming. Based on the type of production, chicken farming is categorized into layer chicken farming and broiler chicken farming. Broiler chickens are used for meat production due to their rapid growth. It takes between six and eight weeks for broiler chickens to be ready for harvesting. It takes longer for layer chickens to be productive. Female chickens start laying eggs when they are 18 weeks old and they will continue to be productive until the age of two years [35].

Different types of chicken require different types of feed. The reason is because the feed plays an important role in the production of high-quality chickens. For example, in order to rapidly form chicken muscle and meat, broiler chickens need feed of higher nutritional value compared to that of layer chickens [36]. This chapter provides a review of the literature of chicken litter production and the use of waste for energy generation.

2.2 Chicken feed

Although all female chickens are able to lay eggs, broiler chickens are domesticated with the goal to produce meat in a relatively short period of time. In order to support the maximum growth, the type as well as the quantity of chicken feed need to be carefully selected. In order to form muscle and meat, broiler chickens have to be fed with feed of high protein and calorie. For additional supplements such as vitamin and mineral, the amount given can be the same as the amount given to layer chickens [35], [36].

By taking age into consideration, the percentage of nutrition composition given to broiler chickens can be categorized into two phases, namely starter phase (1-4 weeks) and finisher phase (4-8 weeks). The composition may consist of 22-24% protein, 2.5% fat, crude fibre 4% crude fibre, 1% calcium (Ca) and 0.7-0.9% phosphor (P). Meanwhile, the composition for the finisher phase may consist of 18.1-21.2 % protein, 2.5% fat, 4.5% crude fibre, 1% calcium (Ca) and 0.7-0.9% phosphor (P) [37]. The percentage of ingredient balance that can be used as reference is displayed in Tabled 2.1.

Table 2. 1 Food balance for the Broiler Chicken, in mass percentage [35].

Feed Ingredients	**Different Aged Broiler**	
	Starter (1-4 weeks)	Finisher (4-8 weeks)
Broken Wheat	47	52
Rice Bran	20	18
Sesame Cake	13	12
Kipper Fish Powder	18	15
Bone Powder	1.25	1
Oyster Shell Powder	–	1.25
Salt	0.5	0.5
Vitamin and mineral	0.25	0.25

Different from broiler chickens that are domesticated for their meat, layer chickens are domesticated for their eggs. Therefore, the feed given will be converted for the maximum growth of egg. In the early growing phase, the nutrition percentage for layer chicks is the same as broiler chicks. Approaching the period of sexual maturity, the percentage of protein and fat needs to be reduced in order to avoid obesity. Entering the laying period, it is necessary to increase calcium up to 4% of the total intake in order to increase the egg production. Table 2.2 is an example of layer chicken diet [38], [39].

In addition to the nutrition contained in the feed, the amount of water fed to chickens also requires attention. Lack of water supply could inhibit growth. For layer chicken in particular, lack of water could result in rapid moulting and decreasing egg production. To balance the high protein content and the forming of fat layer, broiler chickens need more water than layer chickens [35], [40], [41]. Higher water consumption as well as higher protein and fat content results in broiler chickens’ manure that is wetter compared to layer chickens’ manure. The same reason explains why broiler chickens’ manure has higher protein content. The high protein found in the manure of broiler chickens has an additional value as it can be processed to produce another sort of feed for other types of livestock, for example shrimp and fish feed [42], [43].

Table 2. 2 Food balance for the Layer Chicken, in mass percentage [39].

Feed Ingredients	**Different Aged Layer Poultry**		
	Starter (1-4 weeks)	Growing (4-18 weeks)	Egg Laying (18-72 weeks)
Broken Wheat	36	34	32
Wheat Chaff	10	10	10
Broken Rice	10	10	10
Rice Bran	8	15	10
Sesame Cake	12	12	12
Kipper Fish Dust	14	10	12
Dried Molasses	2	2	2
Oyster Dust	2	3	8
Boiled Triticum Aestivum	5	3	3
Salt	0.5	0.5	0.5
Vitamin and mineral	0.5	0.5	0.5

2.3 Chicken bedding material

Bedding materials are normally used in chicken farming. They are useful to cover the bottom part of chicken cage. Covering the cage floor will help chickens to more easily adapt to the environment as the materials resemble natural conditions. Bedding materials help to absorb water vapor that causes the cage to be humid. They also help to absorb the water content of manures. To prevent excessive growth of mould and production of ammonia, damp bedding materials need to be changed regularly [13], [15], [44].

On covered floor type cage, layer chickens require more bedding materials. In addition to serving as the cage floor cover, bedding materials are used to lay eggs. As a result, layer chickens will produce litter containing more organic matters. The most frequently used organic bedding materials are those that come from farming practices such as rice husk, straw and wood shavings [15], [16], [45]. As the composition of chicken litter consists of these organic matters, it can be considered as biomass and can be used as fuel [10], [19], [32].

2.4 Biomass

In the context of energy, biomass refers to carbon-based materials that can be used to produce fuels and/or thermal energy using different conversion methods. These materials include: arable crop residues such as straw or husks, animal manures and slurries and animal bedding materials including poultry litter, grass silage etc. [46], [47].

As there is a wide diversity in the characteristics and properties of these materials, and their various sub-groups, there is also a wide range of conversion technologies to make optimum use of them, which include both biochemical and thermochemical conversion technologies. Anaerobic digestion and microbial fermentation belong to the category of biochemical conversion, while combustion, gasification, and pyrolysis belong to the category of thermochemical conversion [44], [47].

Anaerobic digestion is a breakdown of organic materials. It produces methane (CH_4) and carbon dioxide (CO_2) gas and waste, which can be used as fertilizer. The process is normally performed in an anaerobic digester. Typically, the anaerobic digester is a sealed vessel, where the bacteria for the decomposition of biomass act without oxygen [46], [48].

Combustion is a process of oxidation or burning of flammable materials in the presence of air or oxygen with the release of heat. During the burning of biomass, oxidation is that of predominantly the carbon (C) and hydrogen (H) in the cellulose, hemicellulose, lignin, and other molecules present, to form carbon dioxide (CO_2) and water (H_2O) [49], [50].

Gasification is a partial oxidation process whereby the carbon source such as biomass, is broken down into carbon monoxide (CO) and hydrogen (H_2), plus carbon dioxide (CO_2) and possibly hydrocarbon molecules such as methane (CH_4). This mix of gases is known as synthesis gas (syngas), and the characteristics of the gas will be influenced by the gasification parameters, such as temperature and the oxidizer used. The oxidizer may be air, steam or oxygen [23], [51]–[54].

Pyrolysis is the combination of gasification and combustion without the presence of oxygen. It is essentially based on a long-established process, being the basis of charcoal burning. The products of pyrolysis are syngas, biofuel liquid and char with the proportions of each depending upon the parameters of the process [20], [32], [34], [55].

2.5 Biomass from Chicken Litter

From the four types of meat that is bought by the British public, chicken meat purchase gradually increased by 60% from 1974 through to 2014 (Figure 2.1). In contrast, household purchases of fresh cuts of meat, such as lamb, mutton, pork, beef and veal reduced significantly over the same period. A contributing factor was also the impact of the Bovine Spongiform Encephalopathy (BSE / mad cow disease) crisis, when the public boycotted British beef after a link was established between BSE carried by infected cattle and the human form of the disease, Creutzfeldt-Jakob disease (CJD) [56], [57].

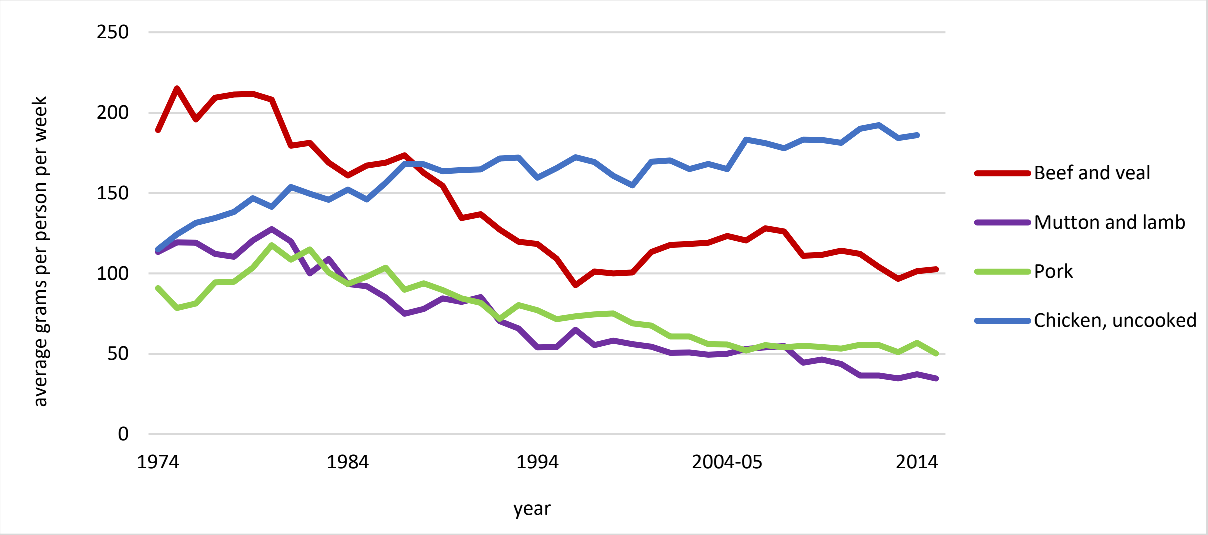


Figure 2. 1 Meat Purchased for UK households, 1974 - 2014 [57].

This trend continued and Defra's Family Food report figures show that the number of poultry slaughtered increased by 4% from 2012 in 2015 reaching 18.4 million per week or around 90 million per year [57].

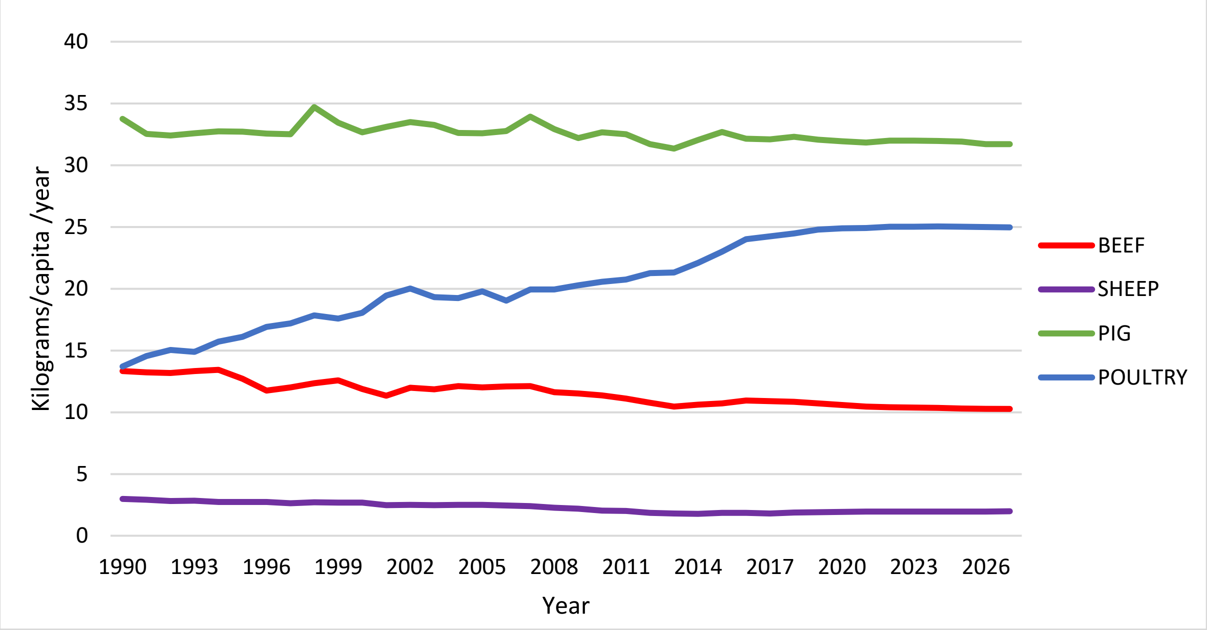


Figure 2. 2 Meat Consumption Indicator for EU countries [58].

The Organization for Economic Co-operation and Development (OECD) projected poultry meat consumption in Europe to remain fairly constant between 2018 and 2026 at approximately 25 kg/capita/year (Figure 2.2). However, in the same period, the projected consumption of poultry meat in Indonesia is expected to keep increasing at around 1% every year compared to other types of meat, which are expected to remain fairly constant (Figure 2.3) [58].

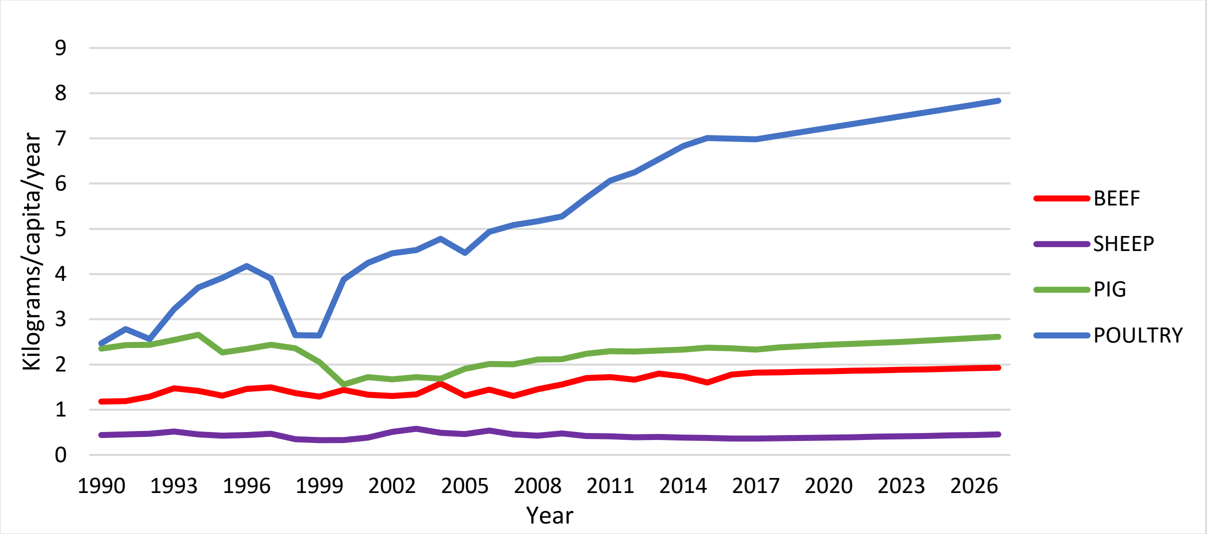


Figure 2. 3 Meat Consumption Indicator for Indonesia [58].

The American Society of Agricultural Engineers (ASAE) standard indicates that manure production by a broiler of approximate weight of 2.36 kg/bird is approximately 4.9 kg during the breeding period (47.7 days) [59]. This means that a single broiler will produce approximately 103.2 gram of manure per day. For the UK, the total annual manure production is approximately 9.2 Ton. Chicken manure can be used as fertilizer on land, but excessive application is restricted to prevent nitrate pollution. This then increases the issues of and cost of waste management [60].

2.5.1 Chicken Litter Utilization

As the world's food production is growing, the demand for fertilizers is also increasing. After World War II, between 1950 and 1980, the use of fertilizer increased from 14 million to 144 million tonnes annually. Presently, China, India, and the United States (US), which are the world's leading grain producers, use more than half the world's consumption of fertilizer (180 million tonness/year). In 2011, the consumption of fertilizer in China reached 50 million tons per year, followed by India (28 million tons/year), and the US (20 million tons/year). On the other hand, the United Kingdom uses less than 2 million tons of fertilizer per year [61]. The world's demand for fertilizer is predicted to reach 203.5 million tons in 2024 [62]. The highest growth rates are found in Africa (4.4% p.a.), especially in Sub-Saharan Africa, not including South Africa, with (6.3% p.a.) [63].

The most common fertilizer employed is chemical. It contains Nitrogen (N), Phosphate (P), and Potash (K). These nutrition elements can actually be found in poultry manure as well, which additionally contains calcium (Ca), magnesium (Mg), and sulphur (S). However, poultry manure also contains ammonia and microbial pathogens, and therefore right treatments must be applied before it can be spread on land to replace chemical fertilizers. Through composting, the issue of pathogens contained in the manure can be addressed, while odours can be prevented by adding 50–55% water vapor [64].

Poultry litter mainly consists of bedding material, feather, and manure. The most common type of bedding used in chicken farming is the biomass type such as hay, straw, wood shavings and rice husk [65]. Since biomass is used as bedding, chicken litter can be converted into useful energy resources. The chicken litter's moisture content significantly affects the conversion method of chicken litter to energy. The moisture content in the combustion method, for example, will inhibit the initial firing and drop the combustion temperature [66], [67].

The characteristics of poultry litter differ depending on the amount of bedding material used. Estimates suggest that for the typical of bedding material use, the volatile solids (VS) content of the poultry litter is derived from the bedding material by approximately 50 per cent by weight and the manure by 50 per cent. Manure and bedding materials have very different properties for energy generation purposes which need to be taken into consideration. For example, the degradability of the VS in the manure fraction in an anaerobic digestion process will be greater than in the bedding fraction (especially for wood-based bedding materials). This is a vital factor to consider when comparing energy generation technologies and bedding materials to match a particular technology [21].

On the dry basis sample, the caloric value of chicken litter is greatly affected by the ratio of ash to volatile solids (VS), and it is expected that the caloric value will be around 17-18 MJ/kg. The chicken litter caloric value is close to the other biomass fuel, such as firewood (dried) has 16 MJ/kg caloric value, lignite has around 10-17 MJ/kg but lower than hard black coal that has caloric value around 23-25 MJ/kg [21].

Fresh chicken manure with high moisture content (70-80%) is not suitable for thermal energy conversion process, particularly combustion process. In addition to adding more bedding materials, a good ventilation control of the chicken sheds also plays a role in decreasing the chicken litter moisture content. With low moisture content (approximately 20%), the caloric value of chicken litter could reach 15 MJ/kg [21].

Currently, poultry litter is primarily used as a replacement for fertiliser and soil ameliorant by a wide range of end users. The over-supply of organic fertiliser is triggering an urgent need for alternative manure treatments. The litter of poultry is either sold as raw (straight from the shed), aged (stockpiled), composted or grinded. However, since the poultry litter has high heating value, it can also be used as an energy generator [68]. The key technologies that can be used to generate energy from poultry litters are anaerobic digestion, combustion and gasification / pyrolysis. Although promising, some of those innovations have not yet been implemented on a commercial scale. By using the waste from chicken farms, costs could not only be managed more economically, but also negative environmental impacts could be reduced [69].

2.5.2 Anaerobic Digestion (Biogas Method)

Countries or areas without hydro or wind resources could consider biomass as a potential source of renewable energy, particularly in areas with significant agricultural and animal wastes [70]. The conversion of biomass into fuel can be classified into two main groups: biochemical conversion and thermochemical conversion. The example of biochemical conversion is anaerobic digestion and microbial fermentation, whereas thermochemical conversion is combustion, gasification and pyrolysis. Both biochemical and thermochemical conversion processes can be used to convert chicken litter into an energy source. However, there are several challenges with both conversion routes [71], [72].

Anaerobic digestion is a way to break down and transform biomass into gas in the absence of oxygen through a biological process. The product is biogas, which is a mixture of carbon dioxide (CO_2) and methane (CH_4). This gas can be used for heating or for generating electricity. Anaerobic digestion is best suited for high moisture content (wet) biomass products [21], [73].

Chicken manure is quite a dry organic waste, and thus a considerable amount of water is needed to convert it into the slurry for anaerobic digestion. In addition, chicken manure has a high content of nitrogen, sulphur and ammonia among other substances that require additional processes for their removal in order for the gas to become suitable for use as a fuel [74], [75].

Accumulation of these substances may cause reactor upset, as indicated by reduced biogas production or possible reactor failure. The composition of the various substances in chicken manure can vary widely depending on the feed and bedding materials and so a detailed characterization of poultry waste is necessary for successful application of anaerobic digestion. It has been suggested that co-digestion with other waste and incorporation of methods to remove or counteract toxicants before anaerobic digestion can significantly improve the waste treatment efficiency [76].

Although ammonia is an essential nutrient for bacterial growth, if present in high concentrations, it can inhibit methanogenesis during the anaerobic digestion process. Ammonia is therefore considered a potential inhibitor during anaerobic digestion, especially when dealing with complex types of substrates like manure or the organic fraction of municipal solid waste [77].

Ammonia is created by biological degradation of nitrogenous substances. Ammonium ion (NH_4 +) and free ammonia (NH_3) are the two principal forms of inorganic ammonia nitrogen. Both forms can cause inhibition in an anaerobic digestion system, directly and indirectly. Free ammonia (FAN) in particular is a potent inhibitor in an anaerobic digester above threshold concentrations. Process inhibition is related to the specific characteristics of the anaerobic digested substrate, pH, process temperature (mesophilic or thermophilic), seed sludge type (inoculum), reactor configuration, and ammonium and ammonia concentrations. This paper addresses the inhibition of ammonia in anaerobic digestion systems and the recovery efforts after inhibition. In addition, the impacts of ammonia inhibition on the microbial population of anaerobic digesters, namely bacteria and archaea, are also assessed in detail [78]. The literature has reported a number of ways of inhibiting the formation of ammonia during anaerobic digestion of poultry litter [79]–[81].

2.5.3 Combustion Method

The simplest method of thermochemical conversion is combustion. Direct biomass combustion has been used to provide heat and power for many centuries, but the overall efficiency of the process is not very high and combustion can also be a source of gaseous pollutants [81]. Basic information is needed to characterize the combustion of agricultural waste including chicken litter, such as the composition, including the moisture content of the substance [67].

Combustion is the process of burning a material with the help of oxygen. The heat generated from the combustion process is used for electricity generation. Coal and a wide range of waste streams have been used to generate electricity by using the combustion method. In Europe and the United States, several commercial plants have used chicken litter as feedstock. A combustion process involves several steps that include [21]:

1. Drying process. The process occurs at the temperature of 100°C with the purpose to evaporate the water contained in chicken litter.
2. Torrefaction process. The process starts at the temperature of 300°C, marked by the devolatilization of chicken litter when the organic volatile compounds start to evaporate. The temperature elevation in this process also causes cellulose and lignin to be separated.

3. When the temperature reaches 800°C, the gasification process takes place. This process generates gases of carbon monoxide (CO) and hydrogen (H_2) (from solid char).
4. Char combustion process. This process occurs when char has been oxidized and transformed into gases of carbon dioxide (CO_2) and CO.
5. Oxidation process. This process takes place at the temperature above 800°C, where volatile gas and tar transform into heat energy.

Compared to the other types of litters, chicken litter contains low moisture and ash. The low moisture and ash content makes chicken litter a suitable feedstock in a combustion process. In order to increase the efficiency, chicken litter can also be mixed with coal that has a higher caloric value. However, chicken litter combustion also poses challenges that include fouling and hazardous gases formation. Moreover, chicken litter combustion also requires a drying process to avoid the initial firing failure. The ash generated from chicken litter burning can be processed into fertilizer because it contains nutrition such as phosphorus (P) and potassium (K) that are useful for plants. However, research regarding the potential of ash have not yet existed. Processing ash into fertilizer can deliver an added economic feasibility for chicken litter. Nevertheless, the feasibility of chicken litter combustion is limited in several ways [21]:

- The large scale of the project facility.
- The amount of chicken litter supply and the transportation from the chicken farming to the facility.
- The cost of chicken litter drying process, affected by moisture content.

A study performed in the US shows that the caloric value of fresh chicken litter (wet) ranged between 7.9 – 14.6 MJ/kg, which would approximately be 15 MJ/kg when it is dry. Meanwhile, the result of another study performed in Australia shows that the caloric value of the studied chicken litter was 17-18 MJ/kg. The difference in the caloric value is caused by the ash content. The chicken litter in the US study had higher ash content and as a result, it had lower caloric value. Both studies reveal that fresh chicken litter combustion delivered electrical energy potential between 0.5 – 1.2 kWh/kg. Electricity generation plants using chicken litter combustion method are highly successful in the UK and US. The plants have the medium capacity between 8 - 60 MW, with the most recent plant that has even a bigger capacity, which is between 35 – 60 MW. The chicken litter combustion is an advanced technology, with numerous facilities that are running as well as being constructed. Therefore, further research and development of this method could be considered unnecessary [21].

In large scale applications, the basic cost and performance of steam plants using co-combustion of biomass and coal is of concern. Co-combustion of biomass with coal is promising, since it combines high efficiency with fair biomass transport distances. Nonetheless, the combustion of biomass is associated with significant emissions, and therefore needs to be improved [82].

Specific fuel properties need to be addressed in order to develop emission reduction steps. Pollutant formation has been shown to occur for two reasons: (1) Incomplete combustion will result in high emissions of unburnt pollutants. Although changes have been made to reduce these emissions by improved furnace design, scope for further optimisation remains. (2) Pollutants and particles originate from constituents of fuel such as N, K, Cl, Ca, Na, Mg, P and S. Biomass furnaces therefore exhibit relatively high nitrogen oxide (NO_X) and submicron emissions. Air staging and fuel staging were developed as the primary NO_X reduction measures offering a reduction potential of 50 to 80 per cent. Key particle reduction steps are not yet established for safe use [83].

Research on combustion properties and thermal kinetics of poultry litter are also relevant to this study. One of the solutions for wet manure is mixing the litter with peat [35]. This mixing can be called a co-combustion. Co-combustion of poultry litter with low quality Turkish lignite has also been studied. Experiments were performed in a thermogravimetric analyser (TGA) under uncontrolled temperature condition. The Ozawa Flynne Walle approach has been used to obtain the activation energy. From the TGA analysis, the activation energy of chicken litter was between 104.4 kJ/ mol and 130.1 kJ/ mol [84].

Different properties of thermal decomposition for poultry litter / coal blends were observed as compared to coal. The thermal properties of the prepared blends showed correlation to the percentage of the sampled poultry litter. In addition, the average activation energies of the blends decreased as the weight percentage (wt%) of coal increased; The lowest activation energy was obtained with 70 wt% litter in the mix. During their co-combustion there was also a synergistic effect between poultry litter and coal samples [84]. Biomass combustion work is limited. This can be due to lack of information regarding the physical and chemical properties of different types of biomass. Research is needed to establish accurate kinetic models to investigate the combustion and emission of biomass [85].

2.5.4 Gasification and Pyrolysis Method

Gasification is a thermal decomposition process that transforms biomass or organic materials into synthesis gas (syngas). Syngas consists mainly of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). Syngas can be used as fuel in electric generator or combined and heat power unit (CHP). Compared to combustion, syngas produces lower carbon emission. Gasification may be an effective technology for chicken litter energy generation, but there are currently few commercial installations worldwide [21].

The steps in a gasification process include [21]:

1. Drying process. This process occurs at the temperature around 100-150°C with the purpose to initiate the evaporation of water that is contained in the chicken litter.
2. Torrefaction process and pyrolysis. This process occurs in the absence or limited oxygen (O_2), at the temperature between 150 - 700°C. It is marked by the chicken litter devolatilization when the organic volatile compounds evaporate. The result of the process is a mixture of anatar gas, tar and char.
3. At the temperature between 700 - 1200°C, the gasification process takes place. With the help of oxygen (O_2), the product of the pyrolysis reacts to char and volatile gases and produces carbon dioxide (CO_2) and water (H_2O).
4. Reduction process. This is the final endothermic reaction where all oxygen (O_2) has been used up to convert water (H_2O), carbon dioxide (CO_2) and the remaining char (carbon, C) into hydrogen (H_2), water (H_2O), methane (CH_4) and carbon monoxide (CO).
5. Oxidation process. This process occurs at temperatures above 800°C where volatile gas and tar transform into heat energy.

The char yield may be used for the heating and drying process of the biomass. The viability of using gasification for chicken litter energy generation is limited by the expense of scrubbing the impurities in the syngas and the processing of ash and potassium, leading to the fusion of tar, which results in increased operating costs for the plant. Nonetheless, there is currently substantial research and development in this field, and further technological advances are likely to occur in the near future [21].

Gasification studies in the US showed that the energy content could be in the order of 6.75MJ/kg litter (with 25 % moisture). In addition, for the output of gas yields of 1.15 Nm3/kg litter, the caloric value is 4.72 MJ / Nm3 (equal to 5.4 MJ / kg)[54]. The value of generation of electricity from poultry litter may be of the order of 0.5 kWh / kg. Chicken litter is rich in value nutrients. While little research investigates the value of char from the processing of gasification, this is an option when using chicken litter as a feedstock. This would however reduce the gasification process's energy efficiency because char would not be available as a feedstock. Further research is still needed in order to investigate the char properties from chicken litter and the economic feasibility of char production. Worldwide, there are very few industrial gaseous schemes that use chicken litter as a fuel source. While the method seems promising, it will take commercial case studies to give the industry confidence to invest in this technology [21].

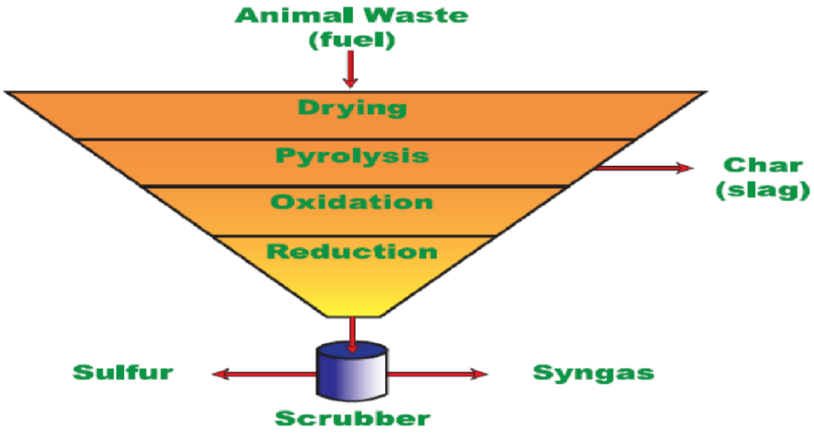


Figure 2. 4 Pyrolysis flow chart showing the major inputs and outputs of the process [21].

Pyrolysis is similar to gasification, which results in the decomposition of a material by heat (below the gasification temperature) in the absence of oxygen (O_2). During the pyrolysis process three primary by-products are produced: Bio-oil, gases (such as methane, ethane and acetylene) and biochar. The main difference from gasification is an absence or lack of oxygen in the process, and oil production in addition to gas. The process of pyrolysis is shown in Figure 2.4. Bio-oil (liquid yield) and gas are the principal energy sources of pyrolysis. The bio-oil properties vary according to the feedstock used and the technology for refining this product is not well advanced [21].

From several studies [21] it is known that gas yield from pyrolysis of biomass may have a calorific value of 15–20 MJ/m^3 and this gas can be used as a fuel of engines and gas turbines directly without any changing. Some studies also reveal that bio-oil from pyrolysis of chicken litter has heating value of 28–29.6 MJ/kg. Pyrolysis feasibility for generating energy from chicken litter is constrained by the state of the technology, the process's relatively lower energy generation capacity, and the biochar's need for a strong revenue stream. Biochar would need to sell for more than $500/ton as an indicator to be feasible, in 2013 the price was $2,580/ton in the US. Also, economic feasibility often requires a stream of revenue to treat the feedstock material (i.e. gate fees). Since chicken litter is a saleable product, feedstock will be a process cost, rather than a source of income [20]. A typical schematic of the pyrolysis process can be seen in Figure 2.5.

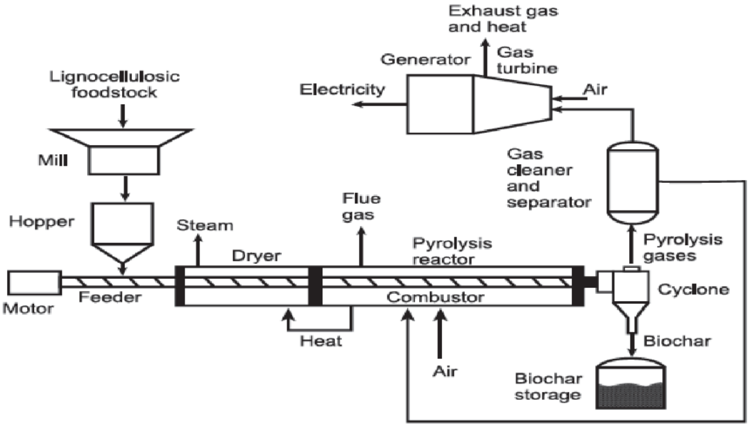


Figure 2. 5 Schematic diagram of a typical plant set-up [20].

Pyrolysis can be generally divided into two types: slow and fast pyrolysis. Slow pyrolysis produces more biochar and less energy, while fast pyrolysis produces more fluid and gas from the same substance, and less biochar. At high temperature and rapid contact time during the process, fast pyrolysis requires small sizes feedstock (< 2mm). Pyrolysis has been the subject of much work, but few commercial-scale facilities actually use this technology. The possibility of using slow pyrolysis to turn chicken litter to energy was studied, and the main product sources were quantified and characterised.

The production of liquid condensates is optimum at 550 °C, which is the fraction that can be converted to liquid fuels. The main component of liquid fraction from this work was identified as fatty acids, N-compounds, phenols and sterols, while water also appears. The fraction of the char has a high energy content but retains most of the sulphur originally present in the substrate and the ashes. Pyrolysis is also associated with a low HHV gas and is considered to be energetically ideal for the process's self-sufficient process. The key potential and vital elements are the use of slow pyrolysis for sanitation and waste-to-energy processing of waste from poultry litters [24].

The poultry litter includes relatively large amounts of ash, which are high in potassium, phosphorus, calcium and magnesium but can be pyrolyzed between 350 and 800^0C and produce a viscous brown biocrude oil with pH about 6 [86]. Fast pyrolysis poultry litter biocrude oils have a much higher calorific value but also a higher nitrogen content than the corresponding biocrude oils from hardwoods. The higher calorific value of the poultry litter biocrude oils appears to be in direct correlation with the raw litter protein content [87].

Also studied are processes of catalytic cracking, hydrodeoxygenation, esterification, supercritical extraction, and vapour reforming. Each upgrade technique has both benefits and drawbacks. Hydrodeoxygenation represents an important phase in the upgrading of bio-oil. While the chemical process is uncertain and requires different unfavourable conditions, this process helps to reduce the oxygen content of raw bio-oil [88]. Different types of catalysts are presented, their limitations and benefits, the use of novel catalysts and the deactivation of catalysts due to char formation under specified conditions for different upgrade techniques. From this study, the researchers conclude that there is no common catalyst for upgrading particular compounds. No particular reaction pathway is established for bio-oil processing. All the reviews and research carried out so far are limited to the individual compounds of bio-oil rather than the whole [88].

There are key points that could be discussed in bio-oil upgrading process study. These include developing multifunctional catalysts that can upgrade the bio-oil properties, becoming able to blend with existing fossil fuels or be used directly as transportation fuels. Bio-oil's potential is increasingly recognised, with rapid growth in research to improve bio-oil properties, especially for dedicated applications and the production of biofuels. Some of the most interesting and potentially useful works on more complex and sophisticated catalytic systems would require more comprehensive development in order to demonstrate feasibility and viability [87].

2.5.5 Relevant Consideration for Choosing Chicken Litter Conversion Technology

Converting chicken litter to energy contributes to the creation of an alternative energy generation as part of the continuing effort to reduce the use of fossil fuels. In addition, using chicken litter delivers the added value of reducing waste from the poultry farming sector. However, there are several factors that need to be considered when generating energy from chicken litter, for example the economic and environment aspects.

2.5.5.1 Economy Issues

Converting chicken litter to energy not only offers a solution for agricultural waste from chicken farming, but also provides an economic added value for farmers and organizations. In general, the use of chicken litter in several models needs an initial capital and running cost that will be used as the foundation for analysing feasibility. The following is an illustration of the economic analysis for using chicken litter through anaerobic digestion, combustion, gasification and pyrolysis process.

Economic Issues with Anaerobic Digestion

Calculating the investment value of the anaerobic digestion model identifies whether the model is profitable or not. One example is taken from a project conducted by Nijhuis Water Technology BV, who built an anaerobic digester for chicken litter in the Ukraine. The digester tank used has the volume of 2000 m^3 that can contain 17 tons of chicken litter per day. If each kilogram of organic chicken litter can produce 0.5 m^3 biogas, then the daily biogas production would be 3400 m^3 per tank. Biogas has the heating value of 23–25 MJ/m^3 or 11.5–12.5 MJ/kg chicken litter. Using a biogas engine, 1 m^3 biogas would produce approximately 2.1 kWh of electricity and 2.5 kWh heat [89].

In this project, the reactor has 10 tanks and chicken litter is not the only material used. Mixed with sorghum, sludge, and waste streams from the chicken slaughterhouse and wastewater for dilution, it can produce 2200 m^3 of biogas in 30 days. The investment value of this project is €13 million with the revenue of €3.6 million/year (3.6 year payback period). The heat value produced by the biogas engine as well as fertilizer produced as the end result of the anaerobic digestion have not been added to the revenue value [89].

In 2017, an anaerobic plant was built in the United Kingdom, with the expectation of overcoming the environmental problem caused by 40,000 tonnes of chicken litter produced each year by poultry sector. The plant has the investment value of £23.3 million and it is expected to generate 3 MW of electrical power that is sufficient to supply 4000 households and to generate high quality organic fertilizer. This plant is the first plant in the world that uses 100% poultry litter with the anaerobic digestion system [90].

Economic Issues with Combustion

The combustion system with boilers using coal as their fuel and poultry litter as the biomass source can be used directly to replace coal. The poultry litter is put into the furnace and it is ignited at high temperature. In the boiler, the high temperature and combustion are used to heat the water into steam. The steam is then used to generate an alternative energy, electrical energy for instance [91]. However, as poultry litter is high in chloride, the combustion process will cause corrosion to the boiler. Maintenance costs for existing boilers, therefore, which are not specially designed for poultry litter, will be extremely high [92].

To install new facilities for poultry litter combustion, the capital cost is estimated to be $10,500/kW with the system capacity of 700 kW (including boiler plant). The annual operating and maintenance cost would be $1,800/kW. The combustion process also has an added value, since the remains of the poultry litter combustion can still be used as fertilizer. All costs are modified into $/kWh to simplify economic measurement. By taking into account the cost of production and the average electricity retail price per kWh is $0.0674 (2006), the payback period is more than 100 years [93].

Economic Issues with Gasification and Pyrolysis

In 2001, a gasification system for poultry litter was already being used with the Biomax Modular Power System. The capital cost used was $1,520/kW for a system with 0.5 MW capacity and $1,121/kW for a system with 1 MW capacity [94]. In 2005, using the Biomax system for forest residues, the capital cost was $2000/kW for a 100 kW system and $1500/kW for a 1 MW system [95]. The payback period of 7.4 to 8.2 years for this gasification system is longer than the anaerobic digestion system but shorter than combustion systems [93].

The conversion of energy using the pyrolysis method requires relatively high heat. Several options are used for this, one of which integrates waste heat using the Organic Rankin Cycle (ORC) [96]. Huang, et al., have performed an economic analysis for pyrolysis using ECLIPSE software to obtain the optimum value of the break-even electricity selling price (BESP). The pyrolysis system used has the chicken litter capacity of 1500 kg/h. If the electrical energy of the ORC system and waste heat are not used, the BESP value would be £218/tonne, while if the electrical energy and waste heat were integrated, the BESP value would decrease to £178/tonne [96].

2.5.5.2 Environmental Issues

Using chicken litter contributes towards alternative energy generation as part of the continuing effort to reduce the use of fossil fuels. In addition, using chicken litter delivers an added value of reducing waste that comes from the poultry farming sector. However, there are several factors that need to be taken into account when generating energy from chicken litter. Besides the economic factors, environmental factors should also be considered. Chicken litter has several characteristics that may deliver a negative impact on the environment. As an example, compare to the cow litter, chicken litter is low in moisture content (15–30%), which means a relatively high volume of water is needed during the process. There is also the issue of high levels of ammonia that can cause an unpleasant odour. The following are several more specific matters that reveal a more comprehensive picture when considering each system for generating energy from chicken litter, namely anaerobic digestion, combustion, gasification and pyrolysis [93].

Environmental Issues with Anaerobic Digestion

Anaerobic digestion is the most natural process to generate biogas. However, there are several matters that need to be considered for anaerobic digestion. Firstly, whether anaerobic digestion is appropriate needs to be considered. Significant amounts of water are needed for poultry litter anaerobic digestion; anaerobic digestion is better suited for layer manure wastes that are high in moisture content. Secondly, the resulting liquid stream, which is rich in phosphate and wet sludge needs to be disposed of. Where land use of poultry litter is not permitted, anaerobic digestion will not alleviate phosphate nutrient disposal requirements. Another aspect that needs to be considered is that anaerobic digestion is a biological process that is time consuming. It includes a longer start-up time (in comparison with combustion and gasification) and reliable, regular maintenance, which will make it more difficult to introduce on a small (on-site) scale [93].

Environmental Issues with Combustion

It is possible for poultry litter to be directly combusted. However, since poultry litter is high in moisture (for combustion process), it needs to be dried to reach below 15% moisture content. Low moisture will result in an optimum combustion process [c]. Following the drying process, the combustion process is performed. This process generates heat, gases such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_x) and sulphur dioxide (SO_2), ashes and fine particles dispersed in the air, and an unpleasant odour [20], [97].

In performing the combustion process, there are some disadvantages that need to be considered. Gases generated through the process of combustion are known to have a negative impact on the environment. Gases such as NO_x and SO_2 may cause acid rain, while gases such as CO and CO_2 contribute to the greenhouse effect in the atmosphere. In addition to issues caused by gases, the small particles dispersed in the air, as well as the odour, may cause air pollution within the surrounding environment. These environmental issues are highly likely to affect humans negatively [98]. In order to decrease the level of air pollution, air pollution control should be considered, using devices like a particulate control system, wet flue gas system or CO_2 capture system [99]. On the other hand, there is also an advantage of the combustion process. Ashes resulting from the process can be used as fertilizer, as they still contain the elements of phosphorus (P) and phosphate (K) [84], [98].

Environmental Issues with Pyrolysis dan Gasification

The pyrolysis process or gasification shares the same negative impact as the combustion process in terms of contributing to air pollution. Pyrolysis generates synthetic gas (syngas) in the form of preliminary carbon monoxide (CO) and hydrogen (H), plus hydrocarbon oil, char and ash. In the combustion process, less syngas results because the oxidation process enables it to be completely combusted into carbon dioxides and water vapor. Pyrolysis generates more syngas because it misses this oxidation process. However, the amount of syngas can be reduced by opting to burn it, which reduces the contribution to air pollution [20], [100].

An advantage of the pyrolysis process comes in the form of bio-oil as its by-product. Bio-oil is generated by using water to condense the syngas produced during pyrolysis. However, a water recycling system is required in areas where water supply is limited [20], [23], [101].

2.5.6 Conclusion: Chicken litter pyrolysis

All countries have agreed to reduce their carbon footprints and the production of greenhouse gasses. One of the ways of reducing the carbon footprint is by switching from fossil fuel consumption to renewable fuel or green energy. Since mad cow disease emerged, meat consumption habits have changed. People have started to eat more chicken meat and the volume of chicken meat consumed has grown enormously. The waste from chickens has now created a new problem, for example the ammonia pollution from chicken manure. Conventionally, to reduce pollution, chicken litter is burned directly.

Based on the literature review, there are three existing methods to generate power from farming waste, particularly from chicken litter. The simplest method is by burning the litter, a method known as combustion. Combustion involves the direct burning of chicken litter and the generated heat can be used for various purposes directly. Another method is anaerobic digestion; bacteria are used to decompose the litter into fertilizers. Methane gas (biogas) is formed during the decomposition process and the biogas can be used as a source of energy. The third method is pyrolysis and involves heating chicken litter in the absence of oxygen. With this method, chicken litter is transformed into biochar and bio-oil. Biochar can be used to improve the soil condition in farms, by enriching the soil with necessary nutrients. Meanwhile, bio-oil can be used as fuel for certain types of engines such as diesel engines, boilers and electric generators.

Of the three mentioned methods, bio-oil, which is the end product of pyrolysis, has the highest value of energy potential, 28–29.6 MJ/kg. Furthermore, in terms of payback period, pyrolysis has the shortest period. Regarding the environmental impacts, pyrolysis may contribute to high air pollution, but this can be reduced by burning the syngas. Based on these findings, this research will focus on the pyrolysis process.

For research purposes, pyrolysis of the chicken litter can be divided mainly into two types: slow and fast pyrolysis. Slow pyrolysis occurs as the main product at low temperature and long residence time (30 min), with char. Fast pyrolysis takes place at high temperatures and very short periods of residence time (0.5–5 s)[102]. The main product of this pyrolysis process is produced in the liquid and gas phases. The liquid phase (bio-oil) holds most of the energy or HHV and is more versatile for storage, upgrading and transportation [23]. Because slow pyrolysis produces high char yields, it is generally more acceptable to process agricultural waste into a char [19]. In addition, inorganic compounds were concentrated in the char. Hence, a slow pyrolysis of chicken litter may produce a soil improver of high quality. It was also estimated that the calorific value of evolved pyrolysis syngas could sustain the energy requirement for the continuous operation of the process [24], [103].

In addition to slow and fast pyrolysis, a third type is intermediate pyrolysis. Intermediate pyrolysis can occur at the same temperatures as slow and fast pyrolysis. The difference lies in the heating rate and residence time, which are 25°C/min and 15–30 min respectively [23]. Due to the longer residence time, the yield from intermediate pyrolysis is more even and it is also recognized to yield higher quality liquid [104].

A comparative analysis of poultry litter pyrolysis in slow, intermediate and fast processes is presented in Table 2.3, from which it can be seen that the yields of biochar and liquids are comparable and in reasonable agreement with previous work. However, a significant difference is evident in the gas yield. Some experiments calculate the gas yield by subtracting the total mass of feedstock with biochar and liquid yield, while in this study (fast pyrolysis), the gas yield is obtained from the gravimetric calculation method [18], [102], [105].

To understand conversion energy in the pyrolysis process requires knowledge of the calorific value of each yield product. Energy produced from the yield product (energy output) can be calculated using the calorific value and the mass of each yield product. Since the char is the majority of yielded product for several pyrolysis cases, the energy from feedstock mainly remains in char [104], [106]. However, overall energy including energy input (energy for running the pyrolysis process), needs to be analysed to justify the pyrolysis process for each application.

Table 2. 3 The comparison of product yield distribution from Chicken Litter Feedstock.

Feed-stock	Pyrolysis type	Temperature (°C)	Biochar (wt%)	Liquid (wt%)	Gas (wt%)	Heating rate (K/min)	Ref.
Poultry litter	Slow	450	42.6	32.4	25.0	23	[16]*
Poultry litter	Slow	500	45.0	35.0	20.0	10	[24]*
Poultry litter	Intermediate	800	32.6	36.8	30.6	25	[107]*
Poultry litter	Fast	600	39.8	23.2	9.9	36000	[17]*
Poultry litter	Fast	550	39.98	26.98	33.04	6600	[102]**
Poultry litter	Fast	530	31.5	27.6	21.9	-	[18]**

*fixed batch reactor, **fluidised bed reactor

2.6 Summary

Among various energy conversion processes known to have been used to convert chicken litter into energy, pyrolysis process is known to be the best as it generates maximum(?) energy output. The caloric value from pyrolysis of chicken litter is higher as compared to the caloric value from other methods of conversion. Pyrolysis is an endothermic process. Consequently, it requires a lot of energy in order to remove the water vapor contained in chicken litter. Chicken litter has low moisture content, and therefore it delivers an advantage as the energy required during the pyrolysis process is lower. The pyrolysis result can be found in chapter 4 and discussed in chapter 5.

CHAPTER 3 Materials and Research Methods

3.1 Introduction

Because of its nutritious contents, chicken litter is widely used as fertilizer for soil improvement. However, when oversupply occurs, chicken litter will accumulate and form nitrates. This issue needs a solution that will enable chicken litter to be processed into another form. The chicken litter originated from chicken farming generally consists of chicken manure, feather, waste feed and bedding materials. The bedding materials commonly used are hay, straw, wood shavings and rice husk. With the purpose of finding a solution for chicken litter processing, a series of experimental tests have been performed [108].

The experiments include slow, intermediate and fast pyrolysis, producing three main yield products: char, synthesis gas (syngas) and liquid (bio-oil). In order to obtain the essential qualities of each pyrolysis process, the elements or compounds present in the yield product need to be determined, alongside the characteristics of the feedstock. With the results of the element/compound analysis, the utilisation of the pyrolysis yield product is simulated with Aspen Plus software.

3.2 Feedstock

The chicken litter feedstock (Figure 3.1) was obtained from several sources including local Irish chicken farms, which is referred to as fresh chicken litter (FCL), and Finnish chicken farms. For research purposes, chicken litter from Finland was supplied and pelletized by Biolan into pellets of 0.5 cm diameter and 1.0 cm length [18], [109], which is referred to as pelletized chicken litter (PCL). Besides chicken litter obtained from chicken farming, a chicken litter model with the composition of 50% (in weight basis) bedding materials and 50% chicken manure was built in order to represent chicken litter of Indonesian origin. Four types of bedding materials: hay, straw, risk husks and wood shavings were used for the research.

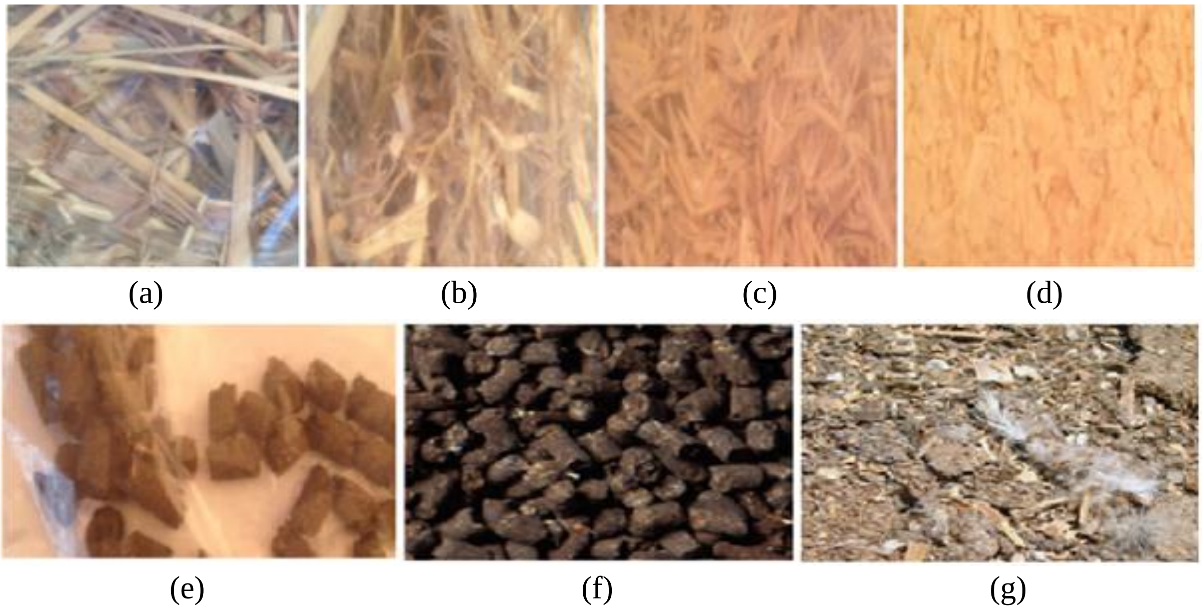


Figure 3. 1 Bedding material and chicken litter, (a) hay, (b) straw, (c) rice husk, (d) wood shavings, (e) chicken manure, (f) pelleted chicken litter, (g) fresh chicken litter.

3.3 Feedstock characterisation

A preliminary test was performed to obtain the characteristics of the chicken litter to be used in the pyrolysis experiment. The test included a proximate analysis test, ultimate analysis test, caloric value test and thermal gravimetric analysis (TGA). The same test was also performed on the solid sample of char that was the product of the pyrolysis process.

3.3.1 Proximate test

The purpose of the proximate test is to obtain the moisture content, volatile matter content, ash content and fixed carbon content of the sample. The proximate test was performed according to either the ASTM D1762-84 standard or BS EN 14774-3, which includes the procedures outlined in the following subsections.

3.3.1.1 Moisture content test

A crucible without the lid is placed in a furnace and heated to 105 °C until it reaches a constant mass. The heated crucible is taken out of the furnace and allowed to cool on a heat-resistant plate before being transferred into a desiccator. The weight of the crucible is noted, before it is loaded with 1.0 g of sample, without the lid, and returned to the furnace at 105 °C for 12 hours or overnight. Duplicates of each sample are made to minimise measurement uncertainty.

Moisture content is calculated using Equation 3.1:

$$MC = \left(\frac{M2-M3}{M2-M1}\right) \times 100\% \quad \ldots\ldots (3.1)$$

Where,
MC is the moisture content (% basis);
M1 is the weight of the empty dry crucible without the lid (grams);
M2 is the weight of the wet sample with the crucible and without the lid (grams); and
M3 is the weight of the dry sample with the crucible and without the lid (grams).

3.3.1.2 Volatile matter content test

A crucible with its lid is placed in a furnace and heated to 900 ± 10 °C (filled with a noble gas like He/Ar to avoid any oxidation) for 7 minutes. The heated crucible is taken out of the furnace oven and allowed to cool on a ceramic plate or a heat-resistant plate before being transferred into the desiccator. The weight of the crucible is noted, and it is loaded with 1.0 g of sample before the lid is added and the crucible and lid are returned to the furnace oven at 900 ± 10 °C for 7 minutes and the furnace heating rate was not set. Duplicates of each sample are made to minimise measurement uncertainty.

Volatile matter content is calculated using Equation 3.2:

$$VM = \left(\frac{M2-M3}{(M2-M1)\times(1-\frac{MC}{100})}\right) \times 100\% \quad \ldots\ldots (3.2)$$

Where,

VM is the volatile matter content (% basis);

M1 is the weight of the empty dry crucible with the lid (grams);

M2 is the weight of sample along with the crucible and lid before volatilisation (grams); and

M3 is the weight of sample along with the crucible and lid after volatilisation (grams).

3.3.1.3 Ash content test

An empty crucible without a lid is placed in a furnace and heated to 550 °C for an hour. The crucible is taken out and placed on a heat-resistant plate for cooling for about 10 minutes before continuing cooling to ambient temperature in a desiccator. The weight of the empty crucible is noted and thereafter the crucible is loaded with 1.0 g of dry sample and put in the cold furnace. The furnace is programmed to reach 250 °C from ambient temperature with a heating rate of 5 °C/minute and is maintained for a further two hours to drive off the volatile matter. After that, the temperature of the furnace is set to 550 °C and the heating rate is increased to 10 °C/minute before it is held at that temperature for another two hours. The sample is taken out and undergoes the same cooling and weighing procedure as that used for an empty crucible. The samples are duplicated to provide better accuracy in results. If the combustion is incomplete – indicated by the appearance of some carbon – then the sample has to be returned to the furnace for another 30 minutes at 550 °C and this process has to be repeated until the mass change is less than 200 mg.

Ash content is calculated using Equation 3.3:

$$A = \left(\frac{M3-M1}{(M2-M1)\times(1-\frac{MC}{100})}\right)\times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.3)}$$

Where,

A is the ash content (% basis);

M1 is the weight of the empty dry crucible without the lid (grams);

M2 is the weight of sample with the crucible and without the lid before ash generation (grams);

M3 is the weight of sample with the crucible and without the lid after ash generation (grams).

3.3.1.4 Fixed carbon content test

Fixed carbon represents the remaining carbon after the complete volatilisation and without the ash content. It was calculated by the difference according to the Equation 3.4:

$$FC = 100 - (MC + VM + A) \quad \ldots\ldots \text{(3.4)}$$

Where,
FC is the fixed carbon content (% basis);
M1 is the moisture content (% basis);
M2 is the volatile matter content (% basis); and
M3 is the ash content (% basis).

3.3.2 Ultimate test

The purpose of this test is to obtain the chemical elements of the sample such as carbon, hydrogen, nitrogen and sulphur (C, H, N and S). All solid sample elements of the feedstock, including char, were identified using a vario EL cube as an elemental analyser. The schematic diagram of the analyser is shown in Figure 3.2. Prior to the sample test, the equipment was calibrated using sulphanilic acid to obtain the standard element composition.

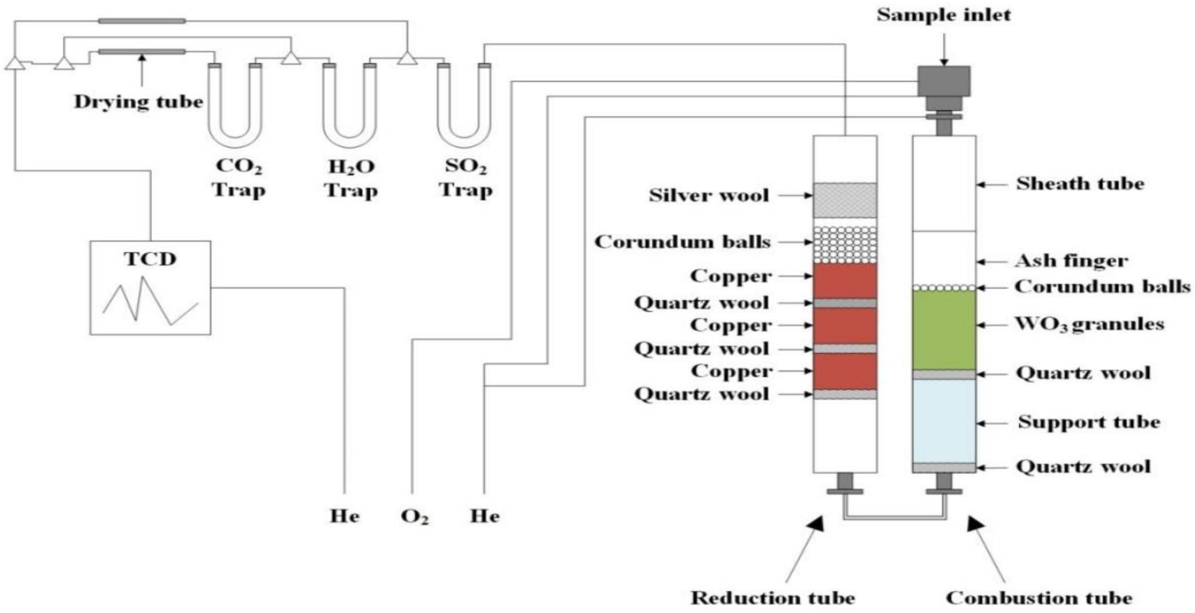


Figure 3. 2 Vario EL cube elemental analyser schematic diagram.

An 8 mg sample was put into the aluminium boats, sealed and squeezed into a small ball before being put in the ball valve above the combustion cylinder and flushed with helium carrier gas. The sample went into the combustion cylinder and was burned with the help of oxygen gas. The emission gas produced was detected by a thermal conductivity detector (TCD) and was used to identify the amount of carbon, hydrogen, nitrogen and sulphur. Meanwhile, oxygen obtained was identified by a difference calculation. The test was done three times for each sample and reported as an average on an as-received basis, dry basis, and a dry and ash-free basis.

3.3.3 Caloric value test

A bomb calorimeter, as shown in Figure 3.3, was used to determine the higher heating value (HHV) of the solid samples. An adiabatic oxygen 6200 isoperibol calorimeter from Parr Instrument Company was used as the bomb calorimeter. Prior to usage, the equipment had been calibrated using a standard sample of benzoic acid. A 1 g sample mass (pressed into a tablet if the sample is in powder form) was put into the sample holder and then into the bomb vessel. It was then sealed and pressurised with oxygen. The bomb vessel was immersed into 2000 ml of water (with temperature maintained at 25 °C). The top cover was closed before an electrical charge was given through the ignition wire to combust the sample. The water temperature was increasing due to the combustion and the increase was recorded to calculate the HHV of the sample.

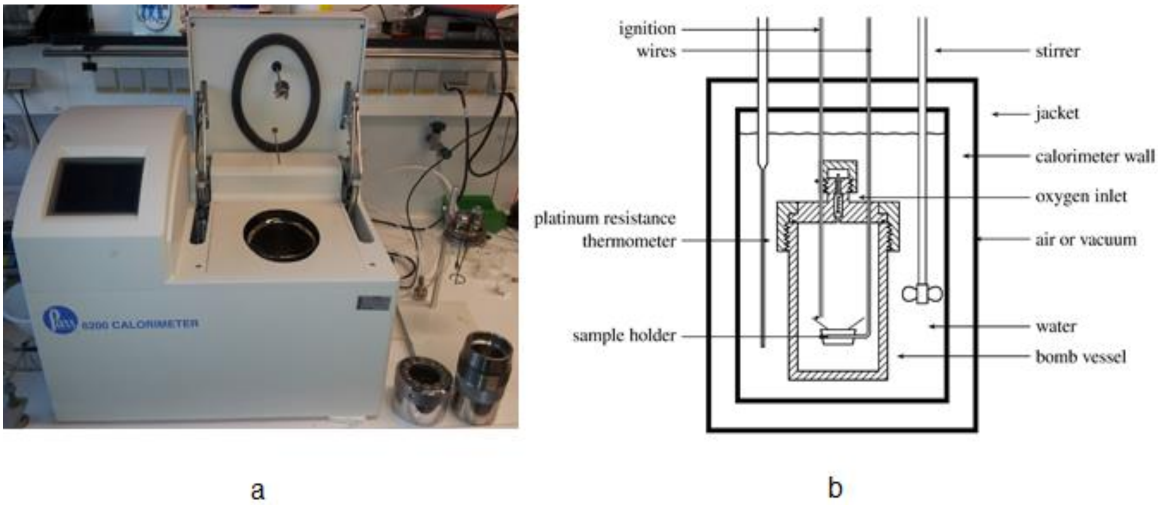


Figure 3. 3 (a) Parr 6200 isoperibol bomb calorimeter, (b) bomb calorimeter schematic.

After the process was finished, the excess pressure of the bomb vessel was released, the bomb vessel was opened and the inner part was cleaned using distilled water. The distilled water that was used for washing was collected into a 50 ml flask and stored for chlorine testing in accordance with the CEN/TS 15408 (2006) standard. Duplicate samples were measured to ensure the precision of the result.

Not all samples had their caloric value measured due to time limitations; however, the caloric value can also be obtained by using an empirical equation such as Equation 3.5 [110]:

$$\mathrm{HHV}\left[\frac{\mathrm{MJ}}{\mathrm{kg}}\right] = (33.5 \times \mathrm{C}) + (142.3 \times \mathrm{H}) - (15.4 \times \mathrm{O}) - (14.5 \times \mathrm{N}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5)$$

Where the numerical value of C, H, O, N is represent the weight percentage of Carbon, Hydrogen, Oxygen and Nitrogen respectively from the sample.

3.3.4 Thermal Gravimetric test

To study the devolatilisation or weight loss of the feedstock due to the temperature elevation, a preliminary test was performed using a thermogravimetric analyser (TGAr) prior to the pyrolysis test (Figure 3.4). A sample was ground to less than 100 µm in particle size, and 10 mg was loaded into the TGA crucible. Using Nitrogen as an inert gas, the sample was heated, ramping up 10°C/minute from room temperature up to 1200°C and was combusted using oxygen gas for the last 15 minutes at a constant 1200°C. All data, including temperature and mass reduction, was recorded in separate computer software, which was transferred into a spreadsheet and used for analysis.

Figure 3. 4 Equipment for thermal gravimetric analysis (TGA).

3.4 Pyrolysis yield analysis

Three main yield products of pyrolysis were analysed using three different methods. The char, as a solid product, was analysed by proximate and ultimate analysis. The procedure methods were similar to those used for the feedstock analysis. For the gas yield, identification and quantification was done using a micro gas chromatograph (Micro GC), while liquid yield was determined using a gas chromatograph mass selective detector (GC MSD).

3.4.1 Gas yield analysis

Evolved gas from the pyrolysis process was condensed and collected into a gas sample bag or syringe prior to the gas analysis. After the pyrolysis process was complete, the gas container was removed and connected to the inlet of the Micro GC directly (no drying process). Micro GC Agilent 3000 (Figure 3.5. (a)) was used to identify and quantify the non-condensable gas from the slow and intermediate pyrolysis (at University of Limerick) and the Varian CP-4900 (Figure 3.5. (b)) was used in a fast pyrolysis process (at TU Delft).

Figure 3. 5 Micro GC (a) Agilent 3000, (b)Varian CP-4900.

(a) (b)

Both Micro GC detectors are able to identify hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). The Agilent 3000 has an additional feature to detect lighter hydrocarbon and gas compounds such as ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2) and hydrogen sulphide (H_2S). All detected chromatograph compounds were calculated using the software from the Micro GC to obtain the quantities.

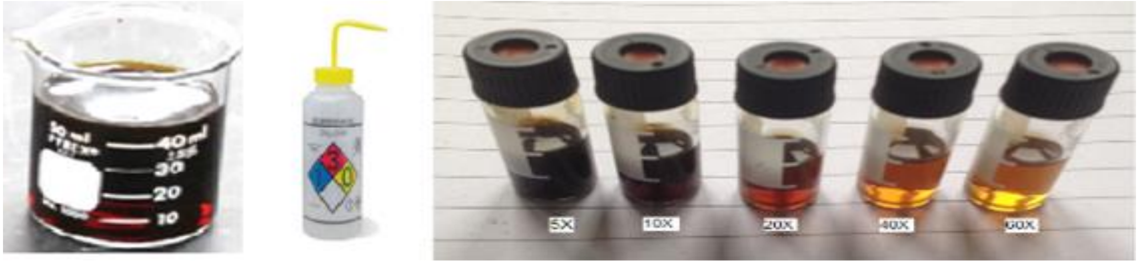
3.4.2 Liquid yield analysis

The compounds of the liquid yield products from the slow and intermediate pyrolysis were identified using an Agilent 7890A GC. When coupled with a triple-axis MSD 5975C, this two-equipment combination is called a gas chromatography mass selective detector (GC MSD) (Figure 3.6). In GC, helium was used as a carrier gas with 1.2 ml/minute constant flow and is mixed with a liquid sample passed through a non-polar HP-5MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness). The injection port in the capillary column operated at 300 °C and the oven temperature program was started at 30°C in 7 minutes, before heating to 180°C at 5°C/minute and finally from 180°C/minute to 270°C at 8°C/minute. The MSD operated in electron ionisation mode at ionisation energy of 70 eV and the full scan mode with the mass range 50–550 m/z. The transfer part between the MSD ion source and the mass analyser of MSD quadrupole was maintained at temperature 300°C [108].

Figure 3. 6 Gas chromatography mass selective detector (GC MSD).

Before the injection of the bio-oil into GC-MSD, it was diluted by using isopropanol. It was divided into several dilution series (5x dilution to 60x dilution), as shown in figure 3.7. To made the 5x dilution, 1 ml oil was added into 4 ml isopropanol, and then for the 10x dilution, 2 ml from 5x dilution was added into 2 ml isopropanol. The steps of making dilution was continued until the 60x dilution. The purpose of the division was to obtain sufficient concentration values and to use the equipment accordingly. For the first measurement, the most diluted oil was used (60x dilution), followed by a less diluted oil, in order to obtain the best result. For the next measurement, the best dilution from the first measurement was used (20 dilution).

Prior to its injection to the GC MSD, liquid yield (bio-oil) was diluted by using isopropanol. As displayed in figure 3.7, the dilution was made into several series, starting from the thickest (5 × dilution) to the lightest (60 × dilution). The first sample that was tested was the liquid yield from the PCL pyrolysis at the temperature of 500°C. For the first measurement, the most-diluted oil was used (60 × dilution), followed by the less-diluted oil. The chromatogram of the GC MSD showed that the bio-oil of 20x dilution delivered the best peak separation. Therefore, the oil yield sample used for the rest of the tests was the one with 20 × dilution.



(a) (b) (c)

Figure 3. 7 (a) Bio-oil, (b) isopropanol, (c) dilution.

The result from the GC MSD enables detection of about 100 species in the liquid yield; however, only 15 of the most-abundant liquid compounds were identified and quantified in this study using the NIST 08 MS library within MSD ChemStation®[108].

3.5 Simulation

Aspen plus software (AspenTech 2019) was used to simulate the pyrolysis process, including the production of the yield at the temperature variation. In Aspen Plus, the simulation is based on mass and energy balance, and is made by unit blocks for reactors, heat exchangers, separators, pumps and compressors. The unit blocks that were used were connected with the stream line, which represents the mass flow, heat flow or work.

The mass stream as mass flow is divided into three classifications: mixed stream, solid stream and non-conventional stream. The solid stream has only solid phase components, while the mixed stream can be a mixture of gases, liquids or solids. The thermodynamic and chemical properties of the solid and mixed streams are provided in the Aspen Plus library. While the thermodynamic properties from non-conventional stream were calculated by Aspen Plus using its proximate, ultimate and sulphate analysis. The details and results of the chicken litter pyrolysis simulation by using Aspen plus software can be found in Chapter 6.

3.6 Summary

The ultimate and proximate analyses, along with the heating value of the poultry litter, were obtained to understand the behaviour of chicken litter for energy conversion. The determination of the devolatilisation behaviour of poultry litter during the heating process was performed by the means of a thermal gravimetric analysis (TGA). The yield of the pyrolysis process was identified and quantified using the appropriate method and equipment. The results from the three pyrolysis methods employed for chicken litter are discussed in Chapter 4.

CHAPTER 4 Pyrolysis experiments

4.1 Introduction

A pyrolysis experiment has been performed using chicken litter as the feedstock employing three types of pyrolysis: slow, intermediate and fast. The slow pyrolysis has been conducted in Brunel University London by utilising the facilities available at the CSEF Research Centre of Mechanical Engineering Department. All experiment results from Brunel University, including intermediate pyrolysis, were tested and evaluated in the University of Limerick, Ireland, using the equipment in the Chemical Science Department, Bernal Institute. Further pyrolysis experiments, used for fast pyrolysis, were performed at the Delft University of Technology (TU Delft), in the Large-Scale Energy Storage Laboratory at the Department of Process & Energy (faculty 3mE).

4.2 Slow pyrolysis

The slow pyrolysis experiment performed at the Institute of Energy Futures, Brunel University, London, lasted for six months. The experimental activities included the design, procurement and installation of all equipment to be used. Based on previously conducted testing, the equipment was divided into two categories: proximate test equipment and pyrolysis test equipment. The proximate test equipment is shown in Figure 4.1.

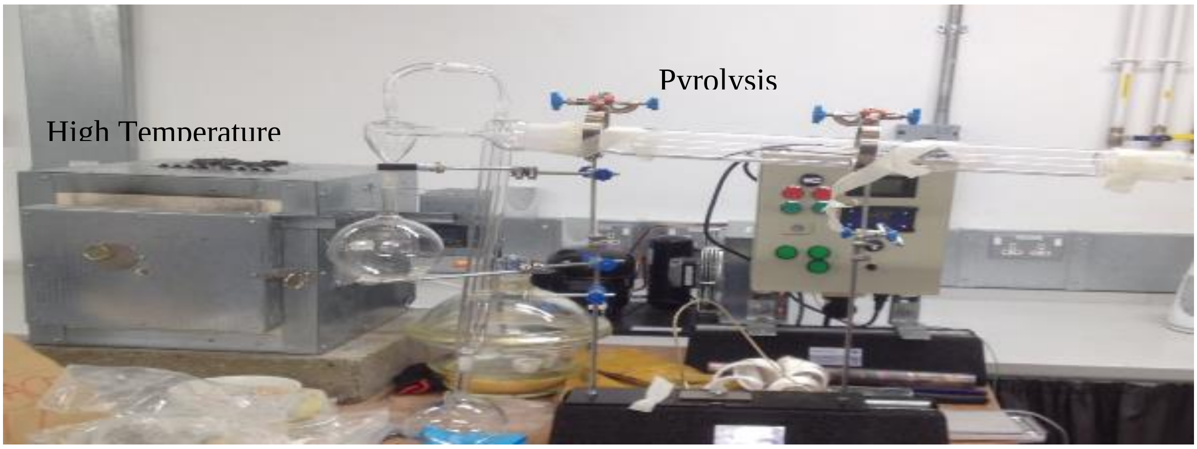


Figure 4. 1 Experimental equipment in CSEF, Brunel University, London.

A high-temperature oven with a maximum temperature of 1100°C was used in the proximate test. The test was performed in order to find out the condition or characteristics of the chicken litter (feedstock) that was going to be pyrolysed. Tests were performed to enable the determination of moisture content (MC), volatile matter content (VM), ash content (A) and fixed carbon content (FC), in weight percentage. The type of feedstock that was tested was chicken litter, with composition of 50% chicken manure and 50% bedding material.

4.2.1 Slow pyrolysis apparatus

The schematic diagram of the pyrolysis apparatus is shown in Figure 4.2. The pyrolysis reactor was manufactured by H. Baumbach & Co. Ltd. [111], UK. It consists of a quartz glass tube reactor and borosilicate glass condensation unit. The diameter of the reactor is 46 mm, while the length is 500 mm. In the condensation unit, raw syngas from the cyclone was cooled through heat exchangers using cold water (5–15 °C) as a heat-transfer liquid. The pyrolysis condensate was collected in two 500 ml flasks and the syngas was collected in the gas-sampling bags (multi-layer aluminium-foil bags). Gas bags were stored in a cold, dry place and it is assumed that no gas compounds leaked in or out during storage.

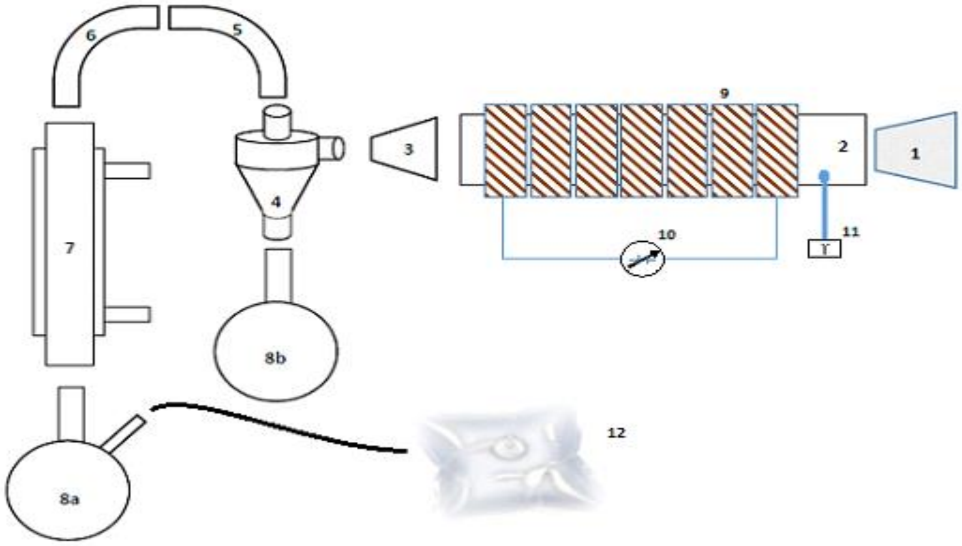


Figure 4. 2 Schematic of the pyrolysis apparatus: (1) stopper, (2) reactor tube, (3) reducer, (4) cyclone, (5) & (6) 90° elbow, (7) condenser, (8a) & (8b) 500 ml flask, (9) heating tape, (10) voltage regulator, (11) thermostat, (12) gas-sampling bag.

The set temperature is achieved and maintained by Samox® heavy insulated heating tape with maximum power output of 1,254 W (Omegalux, USA). The temperature regime in the reactor was measured and controlled by a digital thermostat and voltage regulator (SCR 4,000 W). The control device and electric wiring diagram for the slow pyrolysis experiment is shown in Figure 4.3.

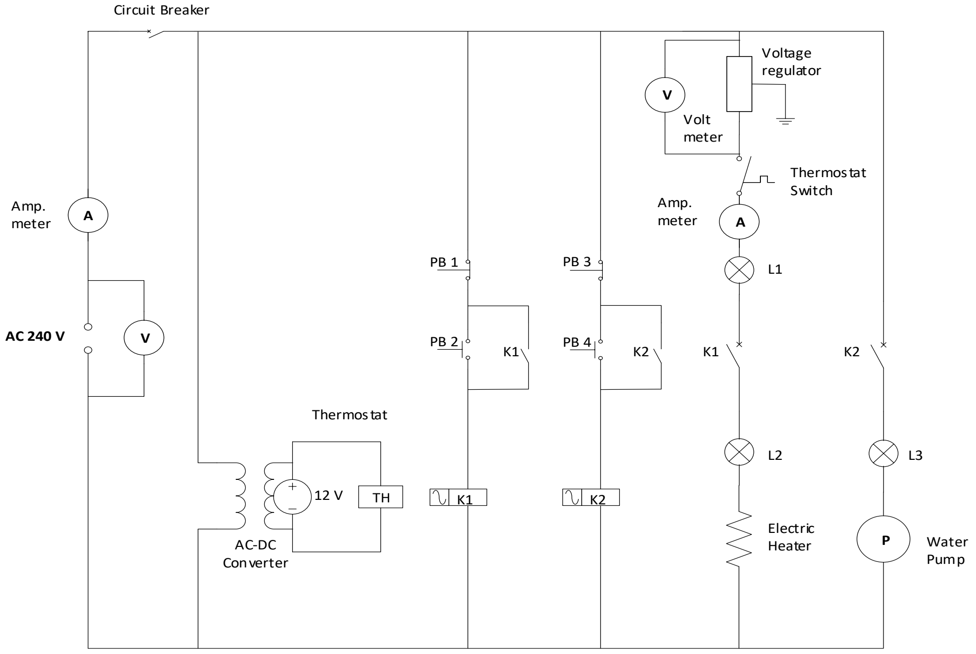


Figure 4. 3 Electric wiring diagram.

4.2.2 Heat required

The slow pyrolysis process for the chicken litter produced three main yields: gas (synthesis gas), char (bio-char) and tar (bio-oil). The energy balance schematic for the pyrolysis system is shown in Figure 4.3. This is used to help the process analysis of the yield produced.

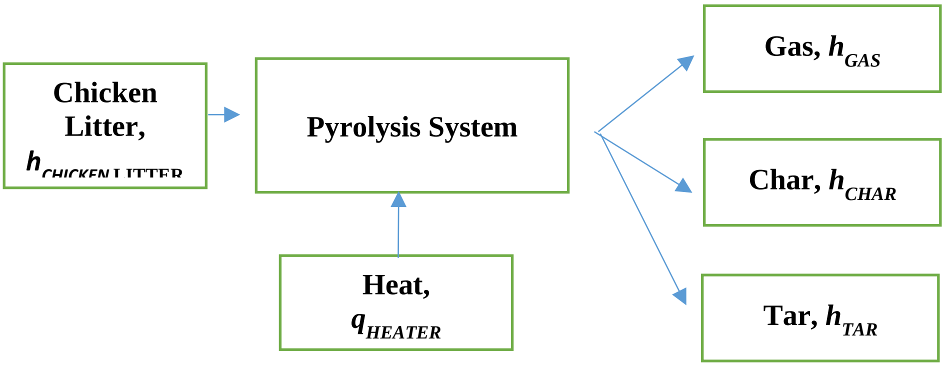


Figure 4.4 Heat balance.

The heat balance in Figure 4.4 shows that the total energy input equals to the total energy output. It can be expressed by Equations 4.1 and 4.2:

$$\sum \text{Specific Energy Input} = \sum \text{Specific Energy Output} \quad \dots\dots\dots\dots\dots\dots \quad (4.1)$$

If the analysis of pyrolysis process is assumed in adiabatic process (no in/out heat) and has reached the steady state condition, then the equation 4.2 can be expressed as follow:

$$h_{CHICKEN\ LITTER} + q_{HEATER} = h_{GAS} + h_{CHAR} + h_{TAR} \quad \dots\dots\dots\dots\dots\dots \quad (4.2)$$

In this case, $h_{CHICKEN\ LITTER}$, h_{GAS}, h_{CHAR}, and h_{TAR} are assumed to be equal to the enthalpy of formation ($\bar{h}^{o}{}_{f}$) of chicken litter, gas, char and tar (bio-oil) respectively. q_{HEATER} is the energy needed to heat the chicken litter (transferred through the wall of reactor tube) during the pyrolysis process; an electric tape heater is used in this case. The reactor tube was covered by the tape heater and the tape heater was insulated. The process to find all enthalpy formations in Equation 4.2 uses the steps outlined in the following subsections.

4.2.2.1 Chemical formula generation

The chemical formula is derived based on the properties obtained from proximate and ultimate analysis of all substances (Table 4.1).

Table 4. 1 Properties of the Substance [101].

Parameter	Chicken Litter	gas	Char	Tar	Relative atomic mass, Ar
moisture (%)	35		4.8	5.3	
pH				2.7	
C (%)	39.5	58.1	47.2	55.3	12
H(%)	4.3	7.2	4.2	6.5	1
N(%)	3.9	8.3	5.5	0.5	14
S(%)	0.8	1.37	0.7	0.05	32
O(%)	27.3	22.7	13.6	37.6	16
Ash(%)	22.9		30.3	0.1	
HHV (MJ/kg)	15.3	27.5	19.9	22.6	
Yield		27%	23%	50%	

The following data in Table 4.2 are the chemical formulae generated from the properties of all substances in Table 4.1.

Table 4. 2 Chemical formula generation.

Substance	Caloric value, HHV		Chemical formulae
	MJ/kg	kJ/mol	
Chicken litter	15.3	1231.4	$C_{3.3}H_{5.6}O_{2.2}$
Gas	27.9	2452.4	$C_{4.9}H_{7.3}O_{1.4}$
Char	19.9	1855.8	$C_{1.2}H_{6.0}O_{1.2}$
Tar	22.64	2251.5	$C_{4.6}H_{6.5}O_{2.4}$

4.2.2.2 Enthalpy balance

The combustion reaction process and enthalpy balance are used to obtain the enthalpy substance according to Equation 4.3.

$$\underbrace{\mathbf{C_aH_bO_c + xO_2}}_{\text{Reactant}} \rightarrow \underbrace{\mathbf{yCO_2 + zH_2O}}_{\text{Product}} \text{ (combustion) } \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4.3)}$$

The enthalpy balance for the combustion process is derived by enthalpy formation in Equation 4.4:

hc = $h_{\text{product}} - h_{\text{reactant}}$ (enthalpy of combustion),

$$h\text{c} = [\, y(\bar{h}^o{}_{f,CO_2}) + z(\bar{h}^o{}_{f,H_2O})] - [(\bar{h}^o{}_{f,C_aH_bO_c}) + x(\bar{h}^o{}_{f,O_2})] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4.4)}$$

If,

$\bar{h}^o{}_{f,O_2} = 0$

hc = HHV substance,

$\bar{h}^o{}_{f,CO_2}$ = -393 kJ/mol,

$\bar{h}^o{}_{f,H_2O}$ = -285 kJ/mol (liquid)

Thus, enthalpy of formation of each substance is shown in the following Table 4.3

Table 4. 3 Enthalpy of formation.

Substance	Chemical formula	Enthalpy formation, $\bar{h}^o{}_f$	
		kJ/mol	kJ/kg
Chicken litter	$C_{3.3}$ $H_{5.6}$ $O_{2.2}$	-860.8	-10695.3
Gas	$C_{4.9}$ $H_{7.3}$ $O_{1.4}$	-693.7	-7776.3
Char	$C_{1.2}$ $H_{6.0}$ $O_{1.2}$	-1225.9	-13145.3
Tar	$C_{4.6}$ $H_{6.5}$ $O_{2.4}$	-496.9	-4997.2

By using Equation 4.2 and the percentage of yield production of the pyrolysis process (in Table 4.1), the q_{HEATER} value is given by:

q_{HEATER} = - 1(-10,695.3) + 0.27(-7776.3) + 0.23(-13,145.3) + 0.5(-4997.2) = 3073.7 kJ/kg

If the mass of chicken litter feedstock for the pyrolysis process, *m*, is 100 grams (0.1 kg) and the handling time for the process is 15 minutes (900 s), then the power input for the electric heater (P_{HEATER}) is found as follows, assuming power factor, *pf* = 0.8:

$P_{HEATER} = q_{HEATER} \times m / (time \times pf)$ = 3073.1 × 0.1 / (900 × 0.8) = 0.427 kW = 427 W.

This calculation was used to select the appropriate electric heater.

4.2.3 Experimental results

The slow pyrolysis tests were carried out at three temperatures: 350, 400, and 450°C. For each pyrolysis test, a batch of 100 g of chicken litter feedstock was placed into the reactor before all parts of the pyrolysis apparatus were assembled. The test was terminated when gas was no longer produced. The duration of the test depended on the setting temperature: approximately 36 minutes at 350°C, 24 minutes at 400°C and 18 minutes at 450°C. The collected liquid and char fractions were weighed and the weight fraction of the gas was calculated by mass balance. The complete combustion process for the feedstock tested would have required around 436 to 496 litres of air, while there are only 0.8 litres of air in the reactor. Therefore, despite the presence of a small amount of air in the reactor at the start of the test, the tests are considered to be conducted in an inert atmosphere, ideally inert gas must be added during the process. The mass percentage of yield production from slow pyrolysis is shown in Table 4.4 and the data is the average from the two sets of experiments.

Table 4. 4 Pyrolysis Test from Brunel University London.

Sample*	Gas (wt%)			Liquid (wt%)			Char (wt%)		
	350°C	400°C	450°C	350°C	400°C	450°C	350°C	400°C	450°C
Hay Mix	20.5	29.4	31.6	27.8	28.7	28.9	51.8	42.0	39.6
Straw Mix	23.3	26.5	31.6	26.0	30.8	29.7	50.7	42.8	38.8
Rice Husk Mix	18.0	22.1	24.8	21.8	30.7	29.2	60.3	47.3	46.1
Wood Shavings Mix	14.1	19.9	23.1	33.1	41.2	39.7	52.9	39.0	37.3

***** Samples were made of 50 % bedding material and 50% chicken manure

4.3 Intermediate pyrolysis

In order to compare several types of feedstock, a pyrolysis experiment was also performed at the Department of Chemical Sciences, Bernal Institute, University of Limerick, Ireland. Two types of feedstock were used: fresh chicken litter (FCL) that was obtained from a local Irish chicken farmer and pelletised chicken litter (PCL) that was collected from a Finnish chicken farm.

4.3.1 Intermediate pyrolysis apparatus

The pyrolysis equipment that was used in the experiment is shown in Figure 4.5. The pyrolysis apparatus includes a cylindrical glass reactor of 45/50 mm, ID/OD and 600 mm in length. The reactor is made of quartz produced by H. Baumbach & Co. Ltd. [111], UK, and is wrapped using Samox® heating tape (940 W maximum power input) to achieve and maintain the pyrolysis temperature [112]. The heating tape was insulated with high-temperature woven fabric and secured with aluminium-foil tape. This experiment used a variety of temperatures: 500°C, 600°C and 700°C, which were controlled by an electro-thermal power regulator type MC227 (Cole-Parmer, UK).

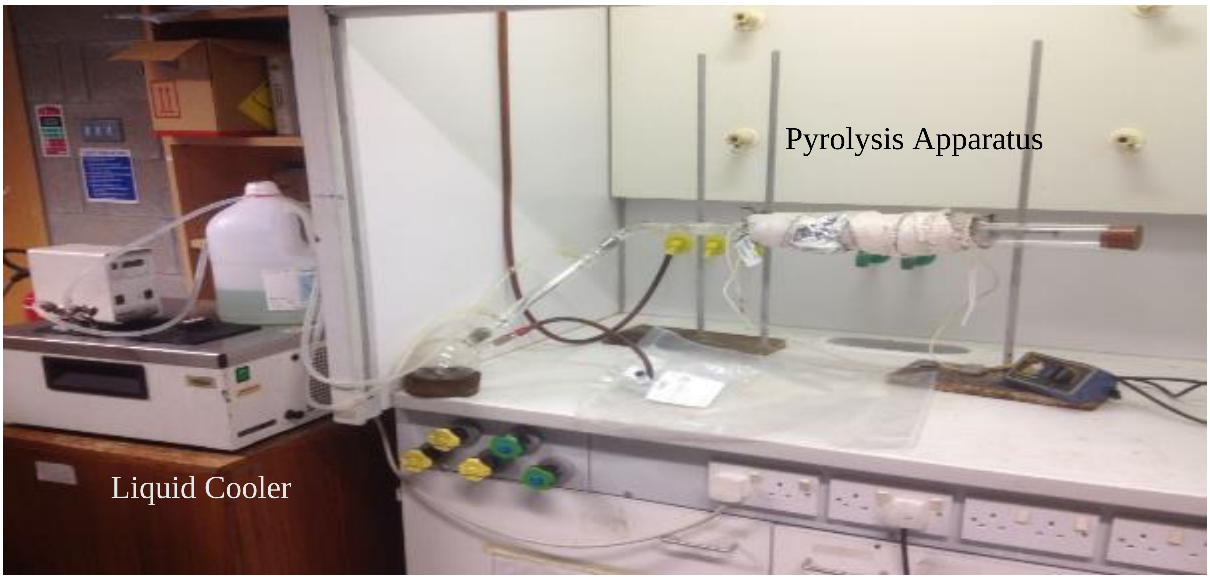


Figure 4. 5 Pyrolysis reactor apparatus and liquid cooler at the University of Limerick.

During the pyrolysis process, in the condensation unit, raw pyrolysis gas from the reactor was cooled down while passing through a condenser cooler with liquid glycol used as a heat-transfer medium. A 500 ml twin-neck flask was used to collect the pyrolysis condensate. The syngas was collected in gas-sampling bags and stored in a cold and dry place prior to gas analysis. It was assumed that no gas compounds leaked during the storage.

The schematic of the pyrolysis is shown in Figure 4.6 and the process was completed according the following procedure:

1. The pyrolyser reactor tube was heated to the required temperature in about an hour. Meanwhile, a metal basket was filled with 50 g of feedstock and inserted into the reactor tube, which was closed by a rubber stopper.
2. Before and during the pyrolysis process, the condenser liquid cooler was maintained at -5 °C.
3. The pyrolysis process was terminated when no visual vapours were observed in the reactor tube. This occurred after 10–12 minutes.
4. The electrothermal regulator was then switched off, the reactor cooled down, and the metal basket with the remaining char was weighed.

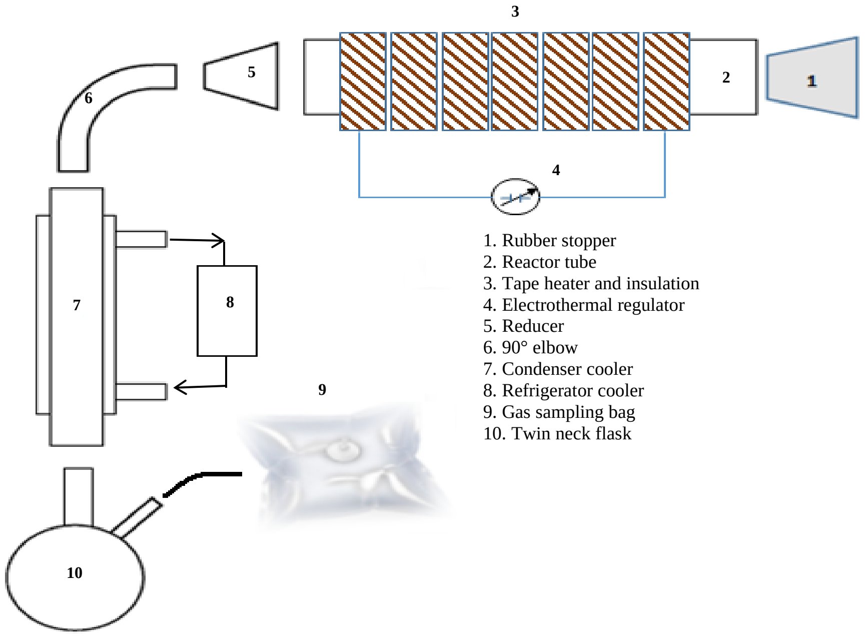


Figure 4. 6 Schematic view of the pyrolyser.

4.3.2 Experimental results

The tests were repeated five times for each temperature regime. Once complete, the apparatus was disconnected and the flask, 90° elbow, reducer, condenser cooler and reactor tube were weighed. To obtain the mass of char and bio-oil yields, all glass components were weighed before and after the experiment and the amount of char was determined from the difference between the weight of the metal basket before and after the experiment and ash that left in the basket was considered as char. The gas yield was calculated by the difference between the initial mass of feedstock and the mass of bio-oil and char. Moisture from wet sample was condensed and add up the bio-oil fraction.

The char yield was weighed after each experiment while the yield of liquid was collected in a flask and weighed after the five experimental repetitions. The experiment was done in 5-time repetition. During the 5-time experiments, only 2 times experiment that the gas yield was collected in gas sampling bags. Meanwhile, in the other 3 experiments, the gas yield was not collected but only passed through a paper-filled plastic bottle in order to trap the remaining bio-oil aerosols in gas. The gas was then released through the exhaust duct. The aerosol weight was added to the liquid yield. The mass percentage of yield production from intermediate pyrolysis is shown in Table 4.5.

Table 4. 5 Pyrolysis test from the University of Limerick.

Sample*	Gas (wt%)			Liquid (wt%)			Char (wt%)		
	500 °C	600 °C	700 °C	500 °C	600 °C	700 °C	500 °C	600 °C	700 °C
PCL	21.4	31.4	39.3	42.8	34.1	30.7	35.8	34.5	30.0
FCL	6.4	33.2	45.2	57.8	42.3	31.8	35.8	24.5	23.0

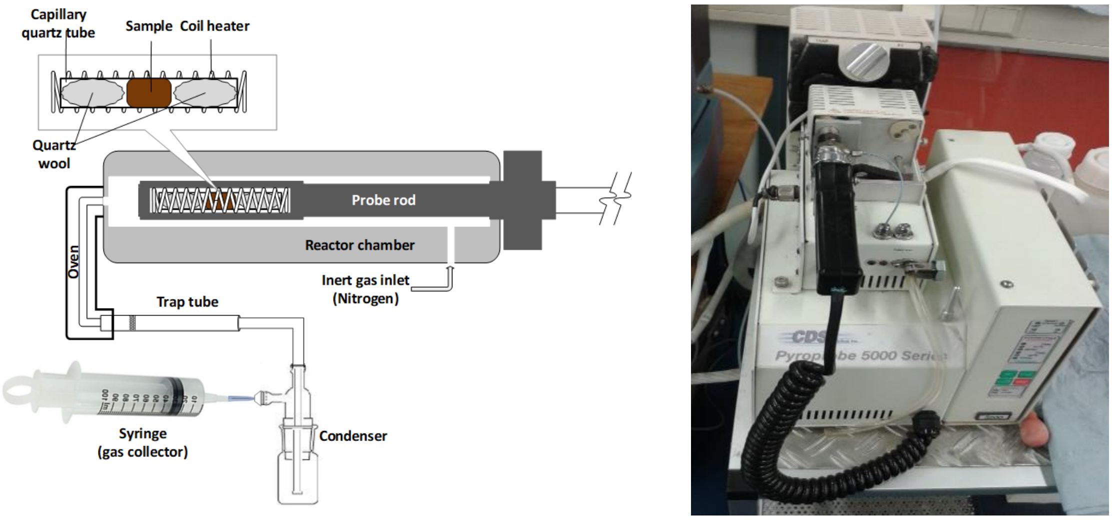
* PCL: pelletised chicken litter; FCL: fresh chicken litter.

4.4 Fast pyrolysis

In order to understand the effect of a fast heating rate for pyrolysis, the feedstock was pyrolysed with a rapid ramping temperature – known as fast pyrolysis. Fast pyrolysis was performed in TU Delft using the facility in their Large-Scale Energy Storage section and was funded by EU Horizon 2020 through the BRISK2 programme. For this short-term research (three-weeks long) only one type of chicken litter was used as the feedstock for all of the TU Delft-based experiments, this was PCL.

4.4.1 Fast pyrolysis apparatus

The fast pyrolysis heating process was performed using a Pyroprobe 5000 series (Figure 4.7 (b)). The heating rate was set at 600°C/second and the regime temperature (pyrolysis temperature) was divided into three setting temperatures: 400, 500, and 600°C. As shown in the schematic diagram in Figure 4.7 (a), 30 mg of ground PCL (< 100 µm) was used as the feedstock and put into a 2.1 mm quartz tube, including quartz wool used as the sample holder, and was then inserted into the tip of the probe rod.



(a) (b)

Figure 4. 7 (a) Schematic diagram, (b) and equipment for fast pyrolysis process.

4.4.2 Experimental Result

During the pyrolysis process, vapour yield product was condensed, with the non-condensable gas collected into the syringe prior to the gas analysis. The scale reading on the syringe showed the volume of the gas. After the pyrolysis process was complete, the syringe was removed and connected to the inlet of a micro gas chromatogram (Micro GC). A Varian CP-4900 Micro GC was used to identify and quantify the non-condensable gas from the pyrolysis process [113]. The Micro GC gives the quantification data of pyrolysis gas in volume base and, by applying the ideal gas law, the mass fraction of the gas can be obtained. The other yield products, char and liquid, were weighed by using scale to obtain the mass. The percentage of each yield product from the fast pyrolysis can be seen in Table 4.6.

Table 4.6 Pyrolysis test from TU Delft.

Temperature (°C)*	Gas (wt%)	Liquid (wt%)	Char (wt%)	Mass closure (wt%)
400	4.4	7.1	62.2	26.3
500	7.2	22.3	48.5	22.0
600	10	23.2	39.8	27.1

* Sample is PCL: pelletised chicken litter.

4.5 Summary

Pyrolysis tests of chicken litter with varying temperature and type of chicken litter feedstock have been conducted successfully. For each experiment, the pyrolysis yield products such as char and liquid were collected and weighed by a scale. During the slow and intermediate pyrolysis, the mass of the gas yield product was obtained by taking the difference between the feedstock and the other yields. Since it was possible to know the gas volume of the yield, the gas from fast pyrolysis was able to be quantified by using micro GC.

The feedstock characteristics and behaviour during the heating process (using a thermogravimetric analyser), including the mass balance of the yield of the char, liquid and syngas, are compared and analysed in Chapter 5. The product yield was analysed using standard equipment to give reliable data. The chemical analysis of the pyrolysis products included gas chromatography, Karl Fisher titration, bomb calorimetry and ultimate analysis.

CHAPTER 5 Results and analysis

5.1 Introduction

During the experiment, chicken litter as feedstock was converted using the thermochemical process of pyrolysis. Based on heating rate, pyrolysis is categorised into three types: slow, intermediate and fast pyrolysis. Using several types of chicken litter, the process of pyrolysis delivered three main product yields: synthesis gas (syngas), pyrolytic liquid and char. The percentage of these yield products varied between pyrolysis processes, depending on the temperature setting. Different temperature settings were applied to obtain the yield product suitable for a certain application.

5.2 Feedstock characterisation

In order to obtain the pyrolysis result that is optimum as well as suitable for the desired application, it is necessary to know the characteristics of the feedstock that is going to be used. Chicken litter proximate analysis is conducted to obtain the characteristics, by using the parameters that include moisture content (M), volatile matter (VM), ash content (A) and fixed carbon (FC). Meanwhile, to obtain the basic element composition such as carbon (C), hydrogen (H), Nitrogen (N), sulphur (S) and oxygen (O), the ultimate analysis is used. The following is the characterisation of the chicken litter used as the feedstock during the pyrolysis experiment.

5.2.1 Proximate and ultimate analyses

The results of both proximate and ultimate analyses of the chicken litter used in the pyrolysis experiment are shown in Tables 5.1 and 5.2. Among the modelled chicken litter types (mixture of bedding and chicken manure), rice husk mix has the highest ash content, which is 30.41%. This indicates that this type of litter will produce more char in a pyrolysis process. Wood shaving mix, on the other hand, is low in ash and high in volatile compounds (23.35% and

64.81% respectively). Consequently, this type of litter will produce more syngas and pyrolytic liquid.

In addition to the modelled chicken litter, two types of chicken litter from farmers were used in the pyrolysis experiment: fresh chicken litter (FCL) and pelletised chicken litter (PCL). After the mechanical process, the moisture content of the PCL was shown to decrease significantly compared to the FCL which had been directly collected from chicken farming: 22.7% versus 4.8%. Similar to rice husk mix, PCL has high ash content and will therefore produce more char than FC L[108], [114]. If syngas were expected to be the end result of a pyrolysis process, then PCL would be more suitable for use than FCL, as it has a relatively high volatile percentage, which is 67.09%.

Table 5. 1 Proximate Analysis of Feedstock. (HHV, Higher Heating Value; MC, Moisture Content; VM, Volatile Matter; A, Ash; FC, Fixed Carbon; FCL, Fresh Chicken Litter; PLC, Pelletised Chicken Litter.)

Sample	**HHV (MJ/kg)***	**MC (wt%)***	**VM (wt%)****	**A (wt%)****	**FC (wt%)****
Hay Mix	14.34	12.98	60.59	24.18	15.23
Straw Mix	12.77	14.55	60.89	26.26	12.85
Rice Husk Mix	12.99	9.09	60.16	30.41	9.43
Wood shavings Mix	14.81	13.05	64.81	23.35	11.84
Chicken Manure	12.51	11.14	57.51	39.01	3.48
FCL	13.75	22.67	56.51	12.70	30.79
PCL	16.28	4.84	67.09	17.92	15.00

*Data are expressed on as received basis, **Data are expressed on a dry basis

Table 5.2 shows that the nitrogen (N) content of chicken manure has the potential to produce higher volumes of ammonia, compared to the other litters analysed. It confirms that adding bedding materials in chicken farming will reduce the effect of air pollution caused by chicken litter. The use of peat for PCL resulted in a higher amount of carbon (C) and hydrogen (H). This explains why the caloric value of the PCL, which is HHV in this case, is higher than that of the FCL. The caloric value of blended chicken litter and chicken manure is obtained using equation 5.1 [110]. The caloric value of FCL and PCL is obtained using bomb calorimetry.

$$\text{HHV}\left[\frac{\text{MJ}}{\text{kg}}\right] = (33.5 \times \text{C}) + (142.3 \times \text{H}) - (15.4 \times \text{O}) - (14.5 \times \text{N}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5.1)$$

Table 5. 2 Ultimate Analysis of Feedstock. (C, carbon; H, hydrogen; N, nitrogen; S, sulphur; O, oxygen; FCL, Fresh Chicken Litter; PCL, Pelletized Chicken Litter.)

Sample	**C (wt%)**	**H (wt%)**	**N (wt%)**	**S (wt%)**	**O* (wt%)**
Hay Mix	52.15	6.09	6.06	0.48	35.21
Straw Mix	51.41	5.97	5.21	0.52	36.88
Rice husk Mix	51.10	6.12	5.15	0.54	37.09
Wood shavings Mix	53.74	6.34	5.07	0.49	34.36
Chicken manure	54.18	6.34	9.64	0.91	28.93
FCL	43.61	3.92	8.28	0.7	0.96
PCL	51.34	6.56	5.42	0.71	0.59

Data are expressed on dry and ash free basis, *Calculated by difference.

5.2.2 Thermogravimetric analysis

Chicken litter can be classified as biomass because it contains the lignocellulose components such as cellulose, hemicellulose and lignin, water, protein and mineral [19], [49], [115]. Thermogravimetric analysis, also known as TGA, was performed to discover the feedstock’s behaviour when heated. The feedstock used for the TGA was PCL, which was ground to particles with a size smaller than 100 μm. The given temperature was started from the room temperature up to 1200°C, with a heating rate of 10°C/min. To finish the process, oxygen was added for the combustion process of the sample.

The mass loss percentage during heating can be seen in Figure 5.1. The rapid decrease in mass started between 200°C and 600°C, which suggests that torrefaction and the pyrolysis process of the feedstock occurs within this temperature range. As seen from the reduction in mass shown in Figure 5.1, pyrolysis seems to occur in two phases, a fast phase and a slow phase. In the slow phase, starting at around 200 °C, hemicellulose is decomposed, followed by cellulose. Lignin starts to decompose in the slower phase, which occurs at around 300 °C [116], [117].

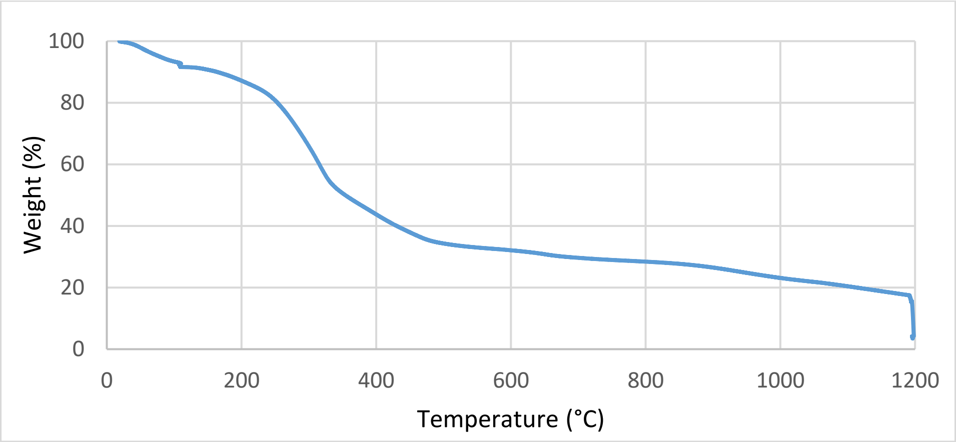


Figure 5. 1 Reduction in Chicken Litter Mass during TGA (wt%).

To identify the speed of feedstock's weight loss against the temperature elevation, the graph in Figure 5.1 has been modified into a differential form and is presented in Figure 5.2. Y-axis in Figure 5.2 is the devolatilization rate, that represented the rate of volatilization process during the elevation temperature where the solid or liquid phase change into vapor because of the high temperature. Figure 5.2 shows two peaks and shoulders, labelled 1–4. Peak 1 shows the drying process where water evaporation is at a maximum, at the temperature of 120°C. Of the lignocellulose components, hemicellulose is the most unstable component thermally, compared to cellulose and lignin [118], [119], causing it to decompose at a low temperature.

Lignin is the most stable component and is decomposed at a high temperature [55], [120], [121]. Shoulder 2 represents the decomposition process of hemicellulose, followed by the decomposition of the hemicellulose components until the maximum condition is reached at peak 3. The decrease in the decomposition rate after peak 3 indicates that the lignin decomposition process is taking place (including protein), which continues to 600°C [122]–[124].; this latter process is shown in shoulder 4. The decomposition process still continues above 600°C, as indicated by small peaks in Figure 5.2. This continuing process indicates that inorganic compounds such as metal carbonates exist to be decomposed until the end of the TGA process [52], [125], [126].

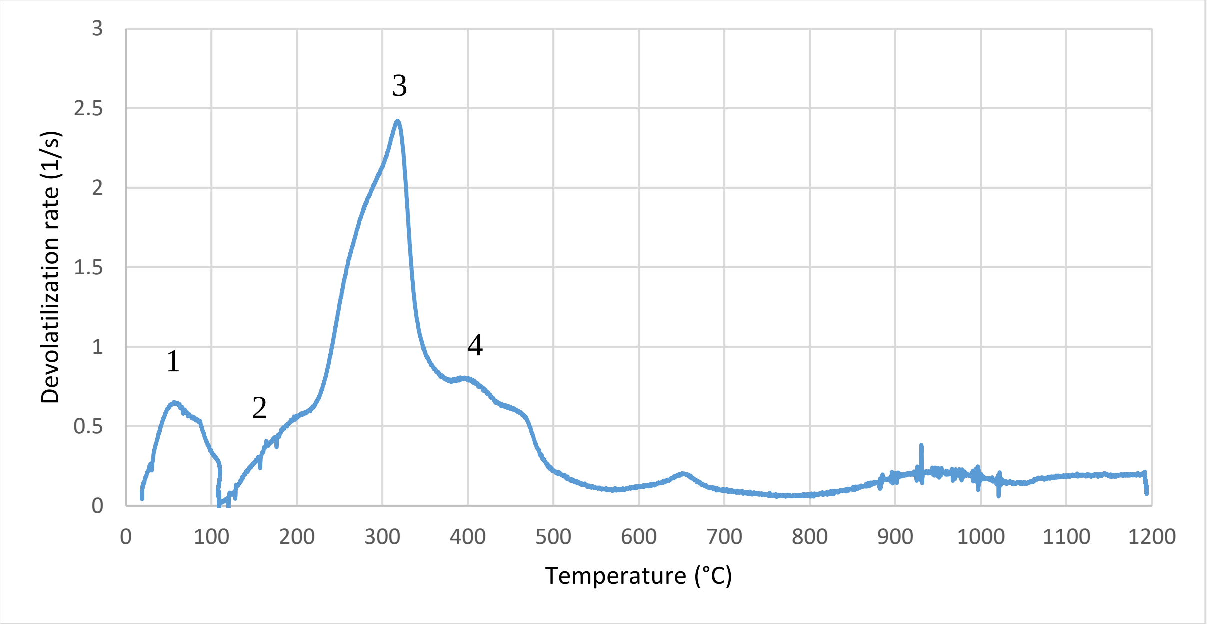


Figure 5. 2 Devolatilization rate of chicken litter in TGA (1/s).

5.3 Slow Pyrolysis Experiment

The slow pyrolysis experiment was performed in an uncontrolled outdoor atmospheric temperature environment. The water used as the heat transfer fluid in the condenser was also uncontrolled and from a supply ranging from 5 to 15°C. The duration of each slow pyrolysis experiment ranged between 18 and 36 minutes, at 350, 400 and 450°C. Several researchers point out that the yield production of slow pyrolysis is char. Details of the percentage of the yield product can be found in the following section.

5.3.1 Yield production

The bar chart in Figure 5.3 shows the distribution of the slow pyrolysis yield production of blended chicken litter (hay mix, straw mix, rice husk mix and wood shaving mix). Each bar represents the mass percentage of each yield product. Temperature and residence time are the parameters that determine the distribution patterns. Figure 5.3 shows that char yield has an identical pattern in each chicken litter type: as the temperature setting rises, the char yield drops [127], [128]. As the temperature increased from 350 °C to 450 °C, the char yield decreased within the range of 14% to 19%. In contrast, syngas yield increased as the pyrolysis temperature rose. At the highest temperature, the maximum syngas production from straw mix was 26.3%. The liquid yield distribution pattern is different. In the experiment using hay mix and straw mix as feedstock, the liquid yield increased as the temperature rose. In contrast, rice husk mix and wood shavings reached a maximum liquid yield of 33.2% and 44.4% respectively, at 400°C.

Chicken litter made up of rice husk has a high ash content and this produces the highest char yields. The char production from the rice husk mix was over 67 wt%, whilst the char yield from wood shavings mix reached around 58 wt% at 350°C. Low char yields from wood shavings mix are correlated to the lowest ash and lower FC content. The highest VM of wood shavings mix resulted in 44.4 wt% liquid yield compared to the other feedstock that produced around 30 wt%. Consistent with the proximate analysis data of the ash component, chicken litter containing rice husk has the highest ash compared to the other types of feedstock used and the high liquid yield generated by wood shavings mix, which reached 44.4% at 40°C, is in line with the higher volatile matter that wood shavings mix contains.

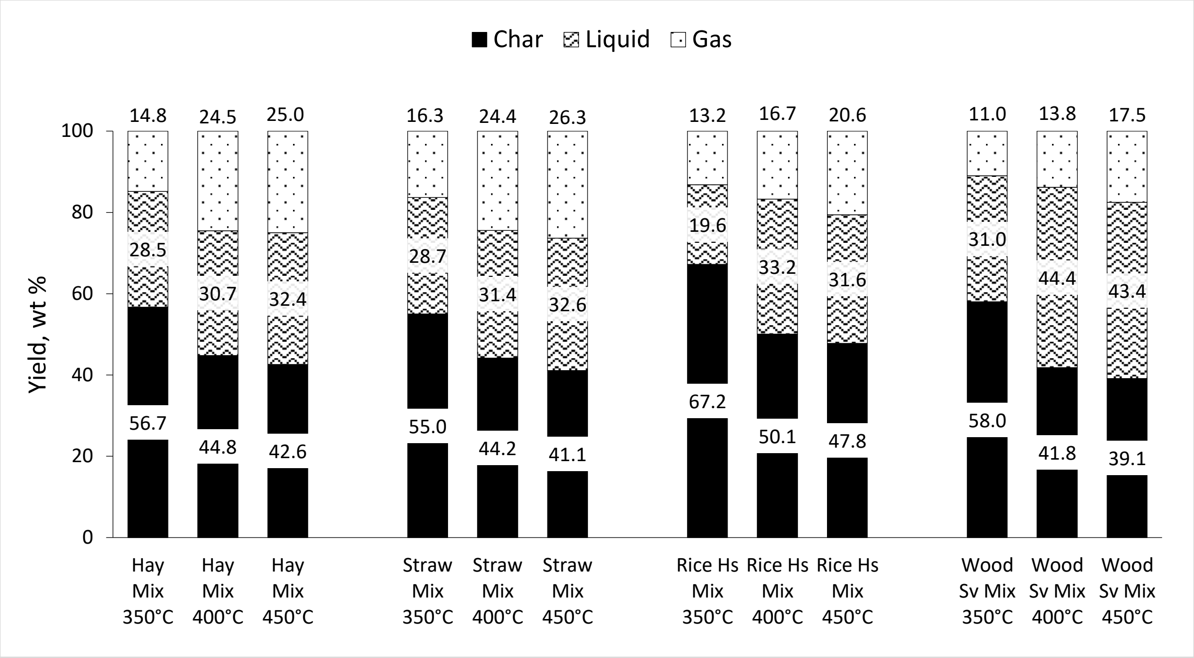


Figure 5. 3 Product yield distribution of four chicken litter feedstocks pyrolyzed at 350, 400, and 450° C. (Rice Hs Mix, Rice Husk Mix: Wood Sv Mix, Wood Shaving Mix.)

5.3.2 Char Yield production

Shown in figure 5.3, The production of char during the slow pyrolysis is affected by the pyrolysis temperature, the char yield is increasing when the pyrolysis temperature decrease. This is because more elements are evaporated at high temperature and resulting the gas and liquid yield. The char yield of rice husk mix in the slow pyrolysis experiment was the highest, reaching 67.2% at 350°C. The lowest char yield of 39.1% resulted from wood shavings pyrolysis at 450°C. This low char yield is to be expected based on the low ash and fixed carbon content.

The changing of char yield in each temperature is followed by the changing char elements composition. The result of measuring CHN (Carbon, Hydrogen, Nitrogen) of char by using ultimate analysis is shown in table 5.3. Because of the increasing pyrolysis temperature, the element of CHN for all char yield from each chicken litter are gradually decline in mass fraction. The highest carbon fraction is 50.89 wt % from char of wood shavings mix at 350°C and the lowest is 35.38 wt% from char of rice husk mix at 450°C. The reduction of CHN elements imply the reduction of caloric value [110].

Table 5. 3 Char yield element from slow pyrolysis (as received basis).

		C (wt%)	**H (wt%)**	**O (wt%)**	**N (wt%)**	**S (wt%)**	**Moisture (wt%)**	**Ash (wt%)**
Hay Mix	**350°C**	46.62	3.55	12.62	3.52	1.49	2.72	29.47
	400°C	49.33	1.5	5.42	1.65	0.25	3.45	38.54
	450°C	42.37	1.97	14.96	2.5	0.27	1.57	36.36
Straw Mix	**350°C**	50.53	1.58	6.55	1.44	0.2	3.54	37.59
	400°C	49.54	2.73	12.22	2.73	0.41	3.1	29.27
	450°C	46.05	2.18	6.09	1.91	0.48	4.08	39.22
RcHusk Mix	**350°C**	46.66	2.34	11.27	1.96	0.35	2.98	34.45
	400°C	44.93	1.46	5.82	1.21	0.14	3.59	42.85
	450°C	35.38	1.81	13.02	1.59	0.27	3.78	44.15
Woodsv Mix	**350°C**	50.89	3.3	15.65	2.52	0.83	2.2	24.61
	400°C	48.68	1.43	10.09	1.26	0.17	3.8	34.58
	450°C	45.85	1.96	10.98	1.95	0.29	2	36.97

5.3.3 Gas Yield Production

Initial identification of gases showed the existence of oxygen and nitrogen compounds. Measurement using the Micro GC showed the amount of nitrogen as between 11 and 25 vol% and oxygen as between 3 and 9 vol%. The nitrogen and oxygen components indicate that some gas entered the reactor during the pyrolysis process. To identify the quantity of the syngas component and directly compare values between each experiment, syngas was quantified in terms of N_2 and O_2 free. This method also avoids the air dilution effect that may cause the small volume percentage of the syngas compound to become unreadable.

The quantification of the gas yield is shown in the bar chart in Figures 5.4 and 5.5, using the unit of volumetric fraction (%). Figure 5.4 shows the dominant yield and Figure 5.5 the less abundant yield. The dominant yield compounds include carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and hydrogen (H_2), while the less abundant yield compounds include ethylene (C_2H_4), ethane (C_2H_6), acetylene (C_2H_2) and hydrogen sulphide (H_2S). The less abundant compounds are those with a percentage of less than 1% [129], [130].

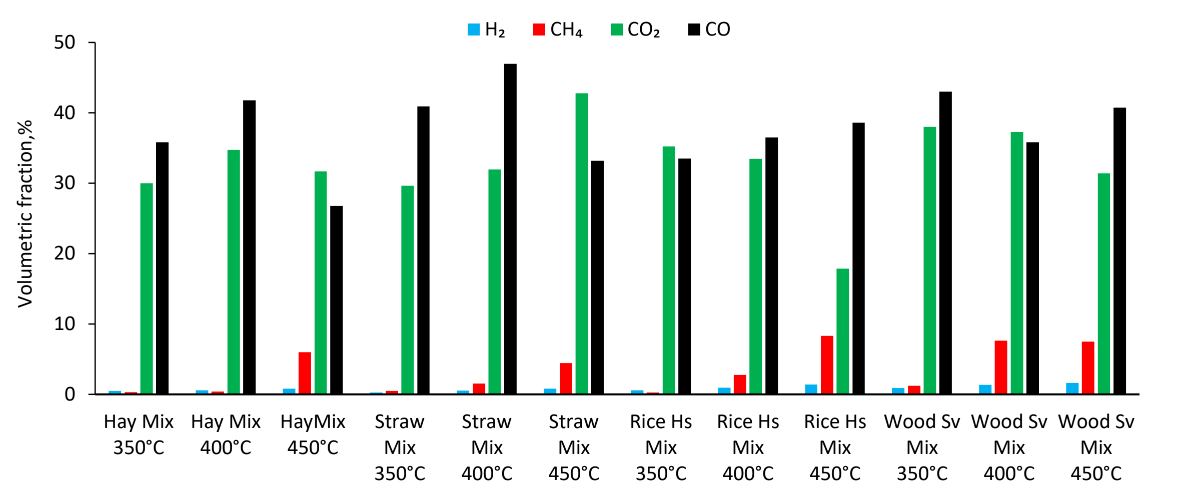


Figure 5. 4 Yields of dominant syngas compounds (vol%). (Rice Hs Mix, Rice Husk Mix: Wood Sv Mix, Wood Shaving Mix; H_2, Hydrogen; CO, Carbon monoxide; CO_2, carbon dioxide; CH_4, Methane; H, Hydrogen.)

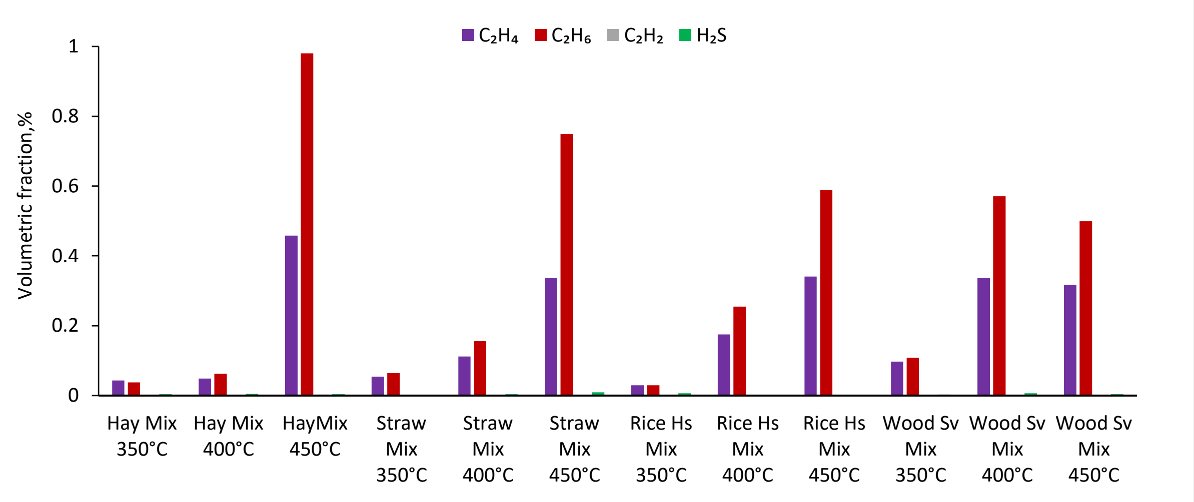


Figure 5.5 Yields of less abundant syngas compounds (vol%). (Rice Hs Mix, Rice Husk Mix; Wood Sv Mix, Wood Shaving Mix; C_2H_4, ethylene; C_2H_6, ethane; C_2H_2, acetylene; H_2S hydrogen sulphide.)

Figure 5.4 shows that the major constituents of the gas produced in chicken litter pyrolysis are carbon monoxide (CO) and carbon dioxide (CO_2). The association trend between the amount of CO and CO_2 produced and temperature increase is not clear. However, in these experiments, the highest carbon monoxide (CO) production was from the straw mix. At the pyrolysis temperature of 400°C, straw mix resulted in 47% of carbon monoxide (CO) production.

Meanwhile, hydrocarbon gases such as CH_4 and the other gases shown in Figure 5.3 reached a maximum production of 8% at 450°C.

5.3.4 Liquid Yield Identification

The proximate analysis results show that each feedstock type contains water, identified through moisture content. During the pyrolysis process, moisture content and volatile matter form vapour, which is later condensed to obtain the pyrolytic yield, when the non-condensable gas becomes syngas (gas yield). The water content in the liquid yield originates not only from wet chicken litter, but also from the thermochemical reaction that occurs during the pyrolysis process. This is confirmed by the high level of water content in the liquid fraction. Using the method of Karl Fisher titration, the water content of the liquid yield was measured to be within the range of 65–72% of the total liquid yield mass.

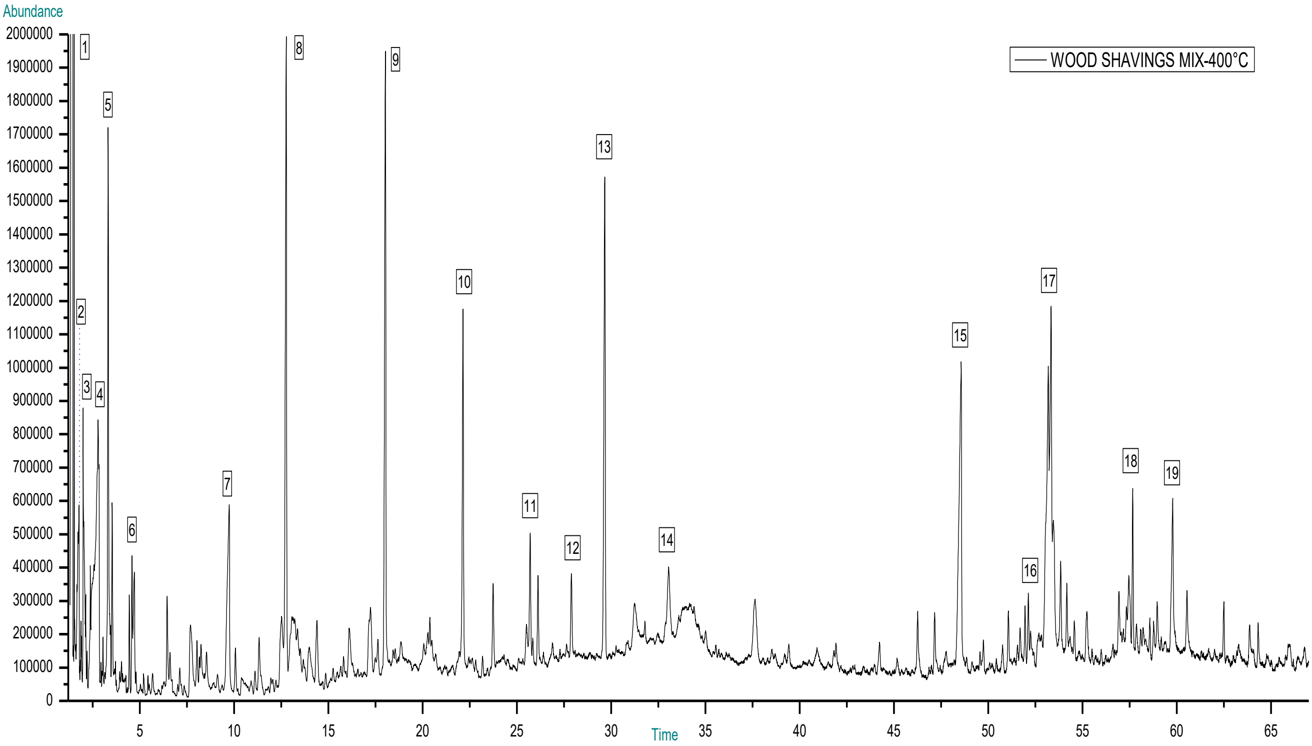


Figure 5. 6 Total ion current (TIC) chromatogram of bio-oil from 400°C pyrolysis of wood shavings mixed with chicken manure.

The identification result of the liquid yield by GC-MSD is shown in chromatogram as displayed in Figure 5.6. The chromatogram shows the total ion current (TIC) of the liquid yield, which resulted from the pyrolysis process of wood shavings mix at 400°C. There are more than 100 species or compounds that can be detected by GC-MSD. However, to represent the liquid yield, the 19 most abundant compounds are chosen. Determining the name of the identified compounds was conducted with the assistance of NIST 08 MS software which is connected to MSD ChemStation® software (the software used by GC-MSD to produce the chromatogram).

Table 5.3 shows the names of the identified compounds. The numbering references are indicated in the chromatogram in Figure 5.6. The production of several species or compounds that form the liquid yield during the pyrolysis process is highly affected by the pyrolysis temperature [131]. Nevertheless, some most abundant compounds such as propanoic acid and phenol family compounds are formed in several liquid yields at various pyrolysis temperatures (350, 400 and 450°C), which shows that the temperature difference in slow pyrolysis does not significantly change the composition of the liquid yield. However, due to long period of storing, oxidation was occurred in all liquid sample. The oxidation possibly had altered the mass/volume fraction of the liquid yield and made the quantification of the liquid yield become inappropriate.

Table 5. 4 Identified bio-oil compounds from 400°C pyrolysis of wood shavings mixed.

Compounds Name	**Compounds Name**
1. Furan, 2,5-dimethyl- (C_6H_8O)	11. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	12. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
3. Pyridine (C_5H_5N)	13. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	14. 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)
5. 2-Furanmethanol ($C_5H_6O_2$)	15. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
6. Pyrazine, 2,6-dimethyl- ($C_6H_8N_2$)	16. 10-Octadecenoic acid, methyl ester ($C_{19}H_{36}O_2$)
7. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	17. Oleic Acid ($C_{18}H_{34}O_2$)
8. Cyclopentanol ($C_5H_{10}O$)	18. Dronabinol ($C_{21}H_{30}O_2$)
9. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	19. Retinoic acid ($C_{20}H_{28}O_2$)
10. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	

Several most abundant compounds as shown in Table 5.3, are consistent with the growth or maturity sequence proposed by Elliot in 1988 [132]. Elliot's observations explain that at the maturity sequence between 400 and 500°C, pyrolytic oil contains mixed oxygenates and phenolic ethers such as acids, aldehydes, ketones, furans, alcohol, phenols, guaiacols and syringols. The liquid yield obtained from the slow pyrolysis in this study contains acids (propanoic acid and butanoic acid), fatty acid (oleic acid) and heterocyclic compounds: pyridines, phenol and its derivative [132], [133].

5.4 Intermediate Pyrolysis Experiment

The intermediate pyrolysis experiment was performed in a benchtop hood without air temperature controller. The range of the face velocity in the benchtop was 3 m/s (60 fpm) and 0.5 m/s (100 fpm), in order to extract gas leaks during the pyrolysis experiment. Using a thermal electro power regulator, the temperature for the pyrolysis experiment was varied, being set at 500, 600 and 700°C. For each pyrolysis temperature setting, polyethylene glycol was used to serve as a cooling medium in the condenser at -5°C. Similar to slow pyrolysis, intermediate pyrolysis resulted in three yield products: gas, liquid and char, and the percentages of each yield are reported in the following sections.

5.4.1 Yield Production

Two types of chicken litter, FCL and PCL were used as the feedstock for the intermediate pyrolysis experiment. The distribution of the resulting yields is shown in Figure 5.7 based on the mass percentage. This is calculated using the feedstock mass as the initial mass reference. The masses of the liquid and char were measured using a weight scale. The gas yield mass was obtained by subtracting the liquid and char yield masses from the total feedstock mass. Yield product difference varied with pyrolysis temperature. However, as shown in Figure 5.7, there is a similar pattern for the yield product of both feedstock types, with liquid and gas being the more dominant yields [65].

Researchers [65], [108], [122] point out that pyrolysis temperature affects the percentage of the yield product. Figure 5.7 shows that as the pyrolysis temperature rises, the liquid and char yields drop. The char yield of FCL drops from 35% at 500°C to 25% at 700°C. The char yield of PCL also drops from 35% at 500°C to 30% at the temperature of 700°C. At pyrolysis temperatures of 500 and 600°C the liquid yield of both chicken litter types is more dominant compared to the other pyrolysis yields (except for PCL at 600°C. In comparison to PCL, the greater production of FCL's liquid yield may be caused by the moisture content, which is 22% of the feedstock mass. Meanwhile, at the highest pyrolysis temperature, which is 700°C, gas yield is dominant. This is because at a high temperature, steam plays an important role in forming volatile matter content of chicken litter. As the pyrolysis temperature rises, gas yield production increases [102], [134]. Figure 5.7 shows that FCL's largest gas yield production is 45.2% at 700°C.

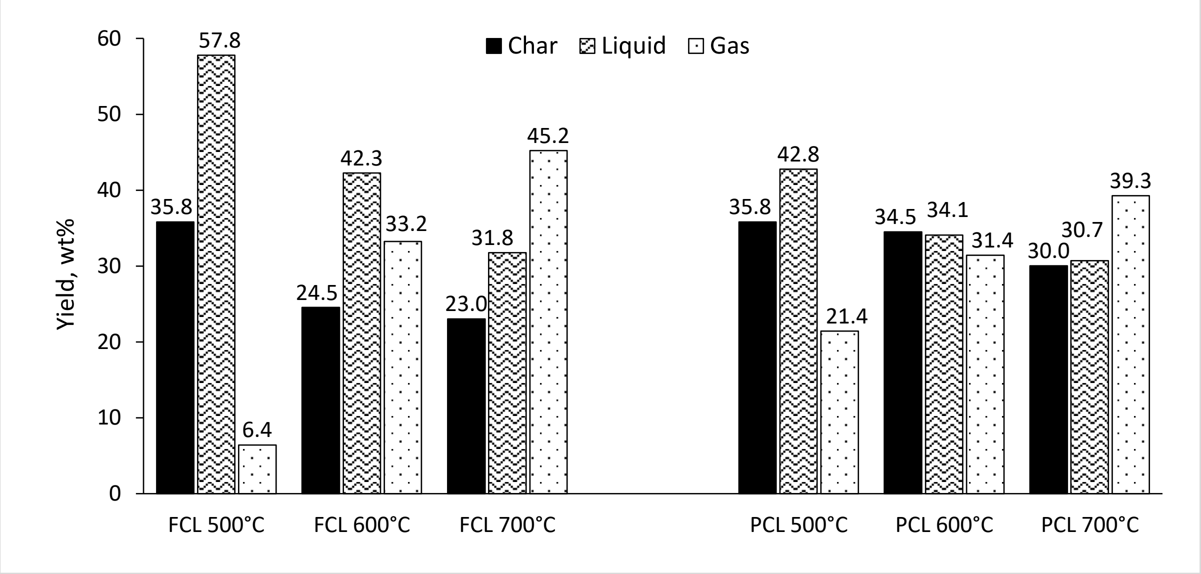


Figure 5. 7 Product yield distribution. (FCL, Fresh Chicken Litter; PCL, Pelletized Chicken Litter.)

5.4.2 Char Yield Production

Figure 5.7 shows that the char yield production drops as the pyrolysis temperature rises, which causes the elemental composition of char to change. The standard test conducted for char yield resulted in the elemental composition of ash in mass percentage and caloric value ('as received' basis) as displayed in Table 5.4. An increase in pyrolysis temperature causes changes in the mass percentage of each element that composes char, such as a decrease in carbon (C), hydrogen (H) and nitrogen (N) elements. This confirms that during high temperature pyrolysis more elements are released from char yield in the form of gas. Similarly, high temperature pyrolysis results in a decrease of the caloric value of char yield, determined empirically from carbon and hydrogen mass.

Observations of several other elements show that pyrolysis temperature variation causes the mass percentage to change. The release of carbon (C) and hydrogen (H) elements from char yield at high temperature shows that the mass percentage of Chlorine (Cl) increased from 1.56% to 1.85% for FCL and from 0.84% to 0.97% for PCL. The char yield's chlorine (Cl) increase shows that the Cl element is part inorganic in origin. It also indicates that high temperature pyrolysis is likely to increase the percentage of inorganic compounds, leading to high production of ash, as displayed in Table 5.4.

Table 5. 4 Ultimate properties and calorific value of char. (FCL, Fresh Chicken Litter; PCL, Pelletized Chicken Litter; HHV, Higher Heating Value).

Elements	FCL char			PCL char		
	500 °C	600 °C	700 °C	500 °C	600 °C	700 °C
Carbon, wt% (db)	58.33	56.12	50.57	52.53	53.37	52.20
Hydrogen, wt% (db)	1.52	1.30	1.12	1.51	1.17	0.55
Oxygen, wt% (db)	1.51	2.78	5.67	6.66	5.65	3.81
Nitrogen, wt% (db)	4.05	2.93	2.45	2.64	2.35	1.96
Sulphur, wt% (db)	0.37	0.60	0.86	0.96	0.98	1.15
Chlorine, wt% (db)	1.56	1.66	1.85	0.84	0.91	0.97
Ash, wt% (db)	32.66	34.61	37.48	34.86	35.57	39.98
HHV [MJ/kg]*	19.31	18.98	18.48	19.30	19.12	18.19

*as received, db – dry basis.

5.4.3 Gas Yield Production

The gas formed in the intermediate pyrolysis experiment was analysed by setting three different pyrolysis temperatures. During the experiment process, the action of changing and inserting the samples into the reactor tube may let some air enter, which becomes trapped in the reactor tube and along the test rig channel. The result of the gas analysis proves that some air did enter the reactor tube, as the components of oxygen and nitrogen were identified by Micro-GC. Similar to the gas yield analysis from slow pyrolysis, the syngas quantification result was determined by normalisation of nitrogen and oxygen free. This decision was made in order to directly compare the syngas components obtained from each experiment, as well as to avoid the dilution effect.

The syngas compounds resulting from the FCL and PCL pyrolysis were identified and then quantified using Micro GC. The quantification result, which can be seen in Figure 5.6, shows that carbon dioxide (CO_2) has the highest volume of gases released during the FCL and PCL pyrolysis processes. The maximum production of carbon monoxide (CO) gas, methane (CH_4) and hydrogen (H_2) occurred at high pyrolysis temperature. This shows that the maximum decomposition of hemicellulose and cellulose occurred at a lower temperature. In contrast, the decomposition process of lignin and the secondary cracking of primary tars occurred at a high pyrolysis temperature.

Several studies show that the formation of heavy hydrocarbon from tar/oil cracking is caused by elevated pyrolysis temperature [18], [118]. Figure 5.6 shows an elevation where the production of CH_4 increases and reaches the maximum amount at the pyrolysis temperature of 700°C. As the light gases volume rises, as shown in Figure 6.7, the production of ethylene (C_2H_4) and acetylene (C_2H_2) gases also significantly increases and reaches the maximum level at the pyrolysis temperature of 700°C. On the contrary, the production of ethane (C_2H_6) and hydrogen sulphide (H_2S) gases decreases at high pyrolysis temperature [18], [135].

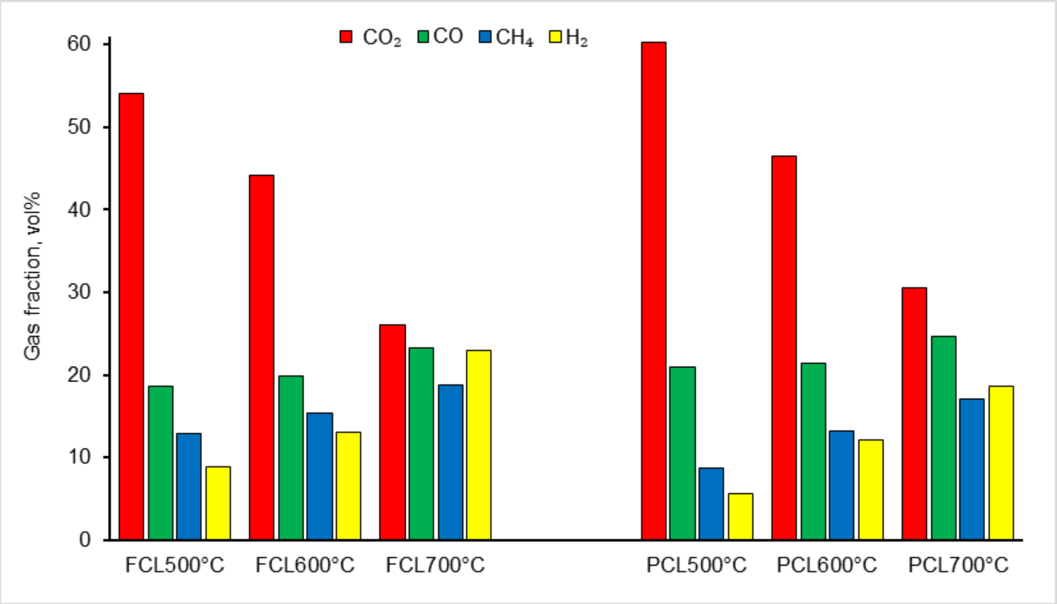


Figure 5. 8 Yields of dominant gas compounds (vol%), carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) and hydrogen (H_2).

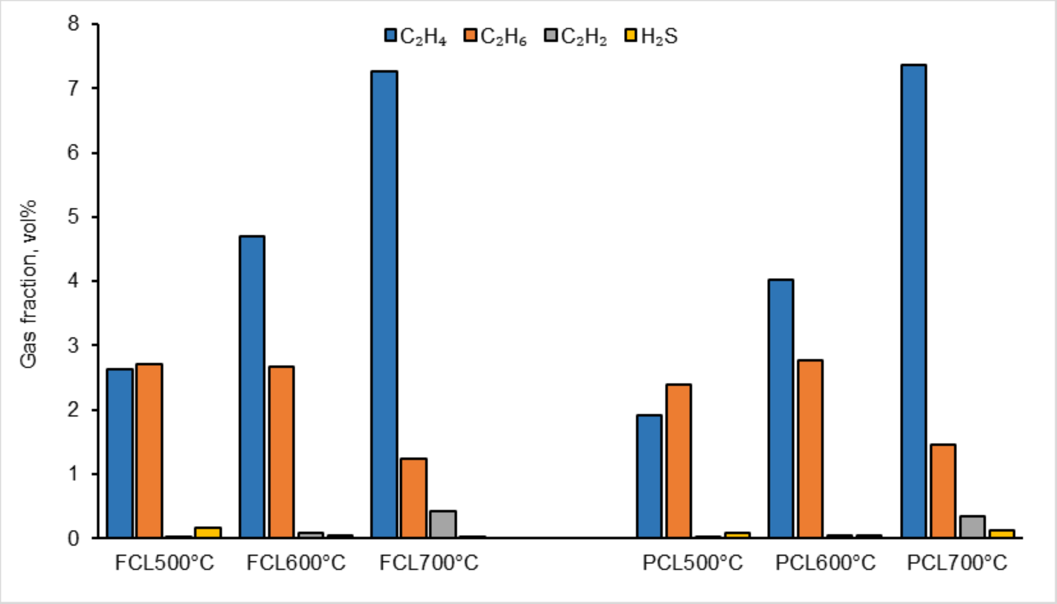


Figure 5. 9 Yields of less abundant syngas compounds (vol%).

The quantification result of the syngas compounds calculated using the Micro GC software is a volume percentage, which can be converted into a mass percentage using the molar weight of each compound. The mass percentage can be used to calculate the gas yield’s composition element. Additionally, the mass percentage of compounds can also be used to modify the caloric value of syngas. Equation 5.2 is used to calculate the caloric value, where f is the volume percentage of the fraction of each compound in syngas [23].

$$HHV = f_{CH_4} \times 35.83 + f_{CO} \times 12.633 + f_{H_2} \times 10.783 + f_{C_2H_4} \times 59.457 + f_{C_2H_6} \times 63.79 \quad \ldots\ldots\ldots\ldots (5.2)$$

Table 5.5 shows the resulting caloric values, modified using mass percentage to obtain the caloric value in the form of mass basis. The results show an increase in caloric value with elevation in pyrolysis temperature.

Table 5.5 Calorific value of gas. (FCL, Fresh Chicken Litter; PCL, Pelletized Chicken Litter; HHV, Higher Heating Value).

	FCL			**PCL**		
	500 °C	600 °C	700 °C	500 °C	600 °C	700 °C
HHV [MJ/kg]	8.876	12.174	19.069	6.613	10.900	16.672

5.4.4 Liquid Yield Production

During the pyrolysis process, water and volatile water formed, which are then condensed into pyrolytic liquid. The pyrolytic liquid is later categorised into liquid yield production. The amount of water content in the liquid yield originated not only from the feedstock (wet chicken litter) but also from the reaction during the pyrolysis process. This is confirmed using a liquid yield's water content test, Karl Fischer titration. The result of the test shows the percentage of water content in the liquid yield, which was 70.8 – 80.4 wt% for the FCL feedstock sample and 73.5 – 78.2 wt% for the PCL feedstock sample.

By using the same method to identify the oil compound in slow pyrolysis, GC-MSD was set to not identify water compound and dilution compound (isopropanol). It was performed this way to obtain an identification result that is water free compound, in other words, only compounds that are composed of oil. Figure 5.10 shows the chromatogram of the GC-MSD identification result for FCL sample at the pyrolysis temperature of 500°C and PCL sample at the pyrolysis temperature of 500 °C.

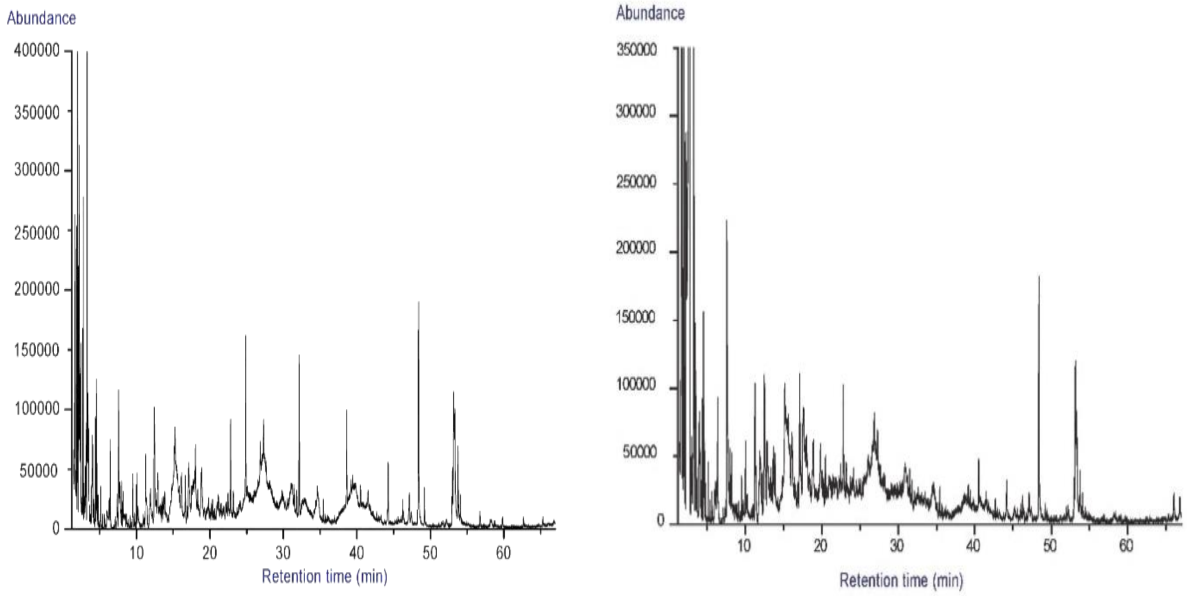


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Figure 5.10 Total ion current (TIC) chromatogram of liquid yield from: (a) Fresh Chicken Litter (FCL) 500 °C, (b) Pelletized Chicken Litter (PCL) 500 °C.

The names of the peaks formed at each retention time can be obtained by using NIST 08 MS and MSD ChemStation® softwares. Table 5.6 shows the names of the oil-composed compounds that can be chosen from the most abundant peaks in Figure 5.10. The quantification calculation for each compound in the oil yield is performed using the integral calculation of each peak area of a compound, and by calibrating it using the phenol calibration curve. The integral calculation of each peak equals the mass of each peak in mg units.

Table 5.6 Most abundant liquid yield compounds from Fresh Chicken Litter (FCL) 500°C and Pelletised Chicken Litter (PCL) 500°C.

Compounds Name	**Retention time (min)**	**Molar mass (g/mol)**	**Compound mass (mg)**
FCL 500°C			
2-Propanoic acid ($C_3H_4O_2$)	1.7	72.1	683.1
Pyridine (C_5H_5N)	1.9	79.1	288.1
Cyclobutene, 2-propenylidene- (C_7H_8)	2.0	92.1	701.1
Acetamide (C_2H_5NO)	2.2	59.0	891.6
Pyrazine, methyl ($C_5H_6N_2$)	2.8	94.1	251.2
2-Furanmethanol ($C_5H_6O_2$)	3.3	98.1	978.3

Pyrazine, 2,5-dimethyl- ($C_6H_8N_2$)	4.6	108.1	297.2
Phenol (C_6H_6O)	7.6	94.1	371.7
Phenol, 3-methyl- (C_7H_8O)	12.4	108.1	489.6
2/3-Trifluoroacetoxydodecane ($C_{14}H_{25}F_3O_2$)	18.0	282.3	254.5
1,4:3,6-Dianhydro-α-d-glucopyranose ($C_6H_8O_4$)	18.9	144.1	285.5
Cyclohexasiloxane, dodecamethyl- ($C_{12}H_{36}O_6Si_6$)	24.9	444.9	358.5
Cycloheptasiloxane, tetradecamethyl- ($C_{14}H_{42}O_7Si_7$)	32.1	519.1	362.8
n-Hexadecanoic acid ($C_{16}H_{32}O_2$)	48.4	256.4	717.4
9,12-Octadecadienoic acid (Z,Z)- ($C_{18}H_{32}O_2$)	53.2	280.4	497.1
PCL 500°C			
Propanoic acid ($C_3H_6O_2$)	1.7	74.1	773.4
Pyridine (C_5H_5N)	1.9	79.1	130.4
Cyclobutene, 2-propenylidene- (C_7H_8)	2.0	92.1	358.7
Butanoic acid ($C_4H_8O_2$)	2.8	88.1	2701.3
2-Furanmethanol ($C_5H_6O_2$)	3.3	98.1	579.0
4-Methylene-5-methylthiomethylcyclohexene ($C_9H_{14}S$)	3.5	154.3	258.5
Pyrazine, 2,5-dimethyl- ($C_6H_8N_2$)	4.6	108.1	150.9
Phenol (C_6H_6O)	7.6	94.1	490.4
2-Pyrrolidinone (C_4H_7NO)	11.9	85.1	220.4
Phenol, 3-methyl- (C_7H_8O)	12.5	108.1	310.3
Phenol, 3-ethyl- ($C_8H_{10}O$)	17.1	122.2	222.2
2-Piperidinone (C_5H_9NO)	17.6	99.1	203.9
Indolizine (C_8H_7N)	22.8	117.2	114.7
n-Hexadecanoic acid ($C_{16}H_{32}O_2$)	48.4	256.4	284.2
9,12-Octadecadienoic acid (Z,Z)- ($C_{18}H_{32}O_2$)	53.2	280.5	245.7

The composition of the liquid yield, as shown in Table 5.6, depends strongly on the pyrolysis temperature [131]. Elliot has published a maturity sequence of pyrolytic oil at the pyrolysis temperatures of 400 to 800°C [132]. According to Elliot, at pyrolysis between 500 and 700°C, pyrolytic oil is composed of phenolic ethers, alkyl phenolics and heterocyclic ethers. In intermediate pyrolysis experiments at the pyrolysis temperature of 500°C, besides short acids such as propanoic acid, liquid yield has heterocyclic aromatic compounds such as pyridines and phenols. At a higher pyrolysis temperature, between 600 and 700°C, several aromatic hydrocarbon compounds such as toluene, styrene, naphthalene and fluoranthene appear. Their production increases at higher temperatures, except for toluene, which did not increase at the temperature of 700°C.

As the pyrolysis temperature increases, the char production decreases considerably. This shows that carbon in the solid phase is evaporated considerably at a high pyrolysis temperature. Most of the carbon element of the feedstock that is evaporated during the pyrolysis process will accumulate to form the compounds that compose the liquid yield [136], [137]. These elements are the primary factor that accounts for the caloric value of the liquid yield. In this study, the caloric value was calculated using the energy balance principle, where the feedstock energy is subtracted from the energy obtained from char and gas yield. The caloric value of the liquid yield is shown in Table 5.7. PCL's liquid yield has a higher caloric value than that of FCL, with the highest value being 19.129 MJ/kg at the pyrolysis temperature of 700°C.

Table 5.7 Caloric value of pyrolysis oil from Fresh Chicken Litter (FCL) and Pelletized Chicken Litter (PCL). (HHV, Higher Heating Volume).

Caloric value	**FCL Pyrolysis**			**PCL Pyrolysis**		
	500°C	600°C	700°C	500°C	600°C	700°C
HHV [MJ/kg]	10.843	11.534	10.491	18.606	18.374	19.129

5.5 Fast pyrolysis experiment

The Pyroprobe 5000 series with an increment of 600°C/s was used during the fast pyrolysis process. Using PCL as the feedstock, the fast pyrolysis was performed at three temperature settings namely 400, 500 and 600°C, without conditioning the environment's air temperature and pressure. The vapour formed was condensed using ice as the heat sink. The uncondensed gas or permanent gas from the pyrolysis process was collected in a syringe for later identification of the compounds and their mass percentages.

5.5.1 Yield production

Figure 5.11 shows the calculated results of all yield productions with the fast pyrolysis method. Figure 5.11 also shows the mass percentage of each yield, compared to the initial mass of the chicken litter. The char mass and liquid yield were calculated gravimetrically using a scale weight. The mass of the gas yield was obtained by converting the volume of each gas yield compound using the ideal gas equation. The volume of the gas yield compound was obtained through quantification performed with Micro GC.

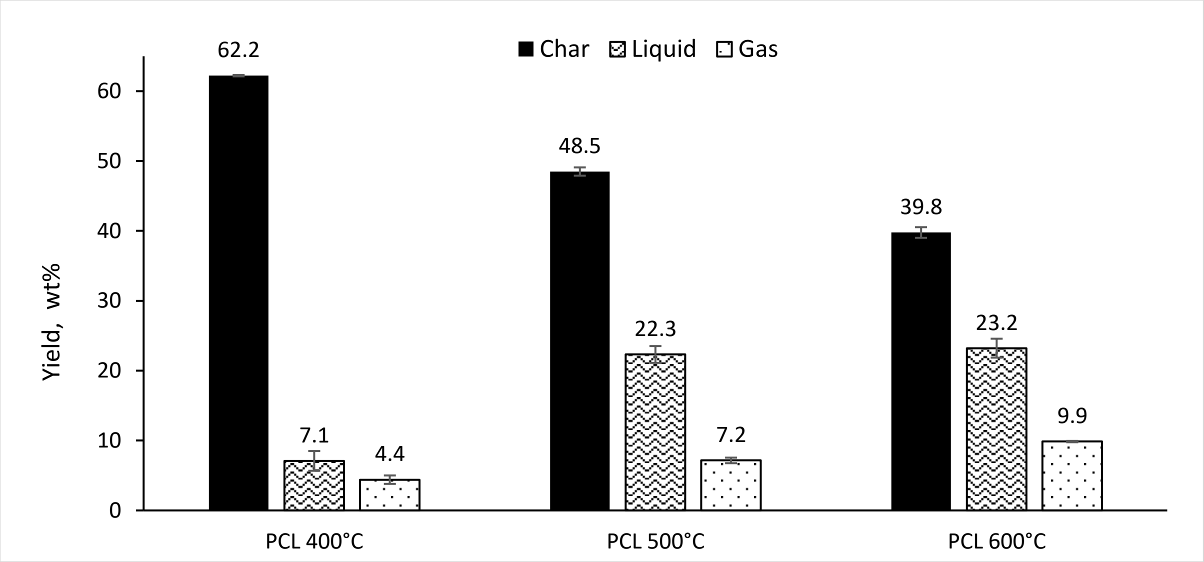

Figure 5. 11 Product Yield Distribution for Pelletized Chicken Litter (PCL) Feedstock pyrolyzed at 400, 500, and 600°C.

Yield production calculation of the mass percentage from the fast pyrolysis experiment at 600°C shows similar results to published research. Table 5.8 shows the analysis comparisons of the yield productions. The amount of char and liquid yield from the three experiments are close, however, there is a significant difference in the gas yield production. The difference is caused by the use of a different method to obtain the amount of yield production. The gas yield was obtained by subtracting the weight of the feedstock with the weight of the char and liquid yield [29]. Meanwhile, in another study [30] and this study, the calculation for each yield is done by using the gravimetric method, which is calculated based on the quantification data from Micro-GC equipment.

Table 5. 8 The comparison of product yield distribution for poultry litter feedstock.

Temperature (°C)	Char (wt%)	Liquid (wt%)	Gas (wt%)	Source
600	39.8	23.2	9.9	This study
550	39.98	26.98	33.04	[29]*
530	31.5	27.6	21.9	[30]*

*fluidised bed reactor

The total percentage of the weight of the yield production (char, liquid and gas) in this study does not reach 100%, approximately 72.9% in total, and the rest of 27.1% may be caused by the release of light gases during the dissembling process of the pyroprobe equipment at the end of each experiment. In addition, several gases such as hydrocarbon gas (C_2H_4, C_2H_6,), NH_3, and gas species that contain sulphur were also not measured. Besides in gas yield, the loss in liquid yield may also be caused by loss of air during the experiment. Moreover, it was known that some oil was stuck on the inner walls of the pyroprobe oven. It could be seen during the process of deep cleaning the pyroprobe at the end of the experiment [113].

5.5.2 Char yield production

Similar to the previously conducted pyrolysis process, the percentages of the yield production show a similar pattern. Different pyrolysis temperatures result in different yields; high char yield production occurs at lower pyrolysis temperature while more liquid and gas yields occur at higher pyrolysis temperature [127], [128]. A significant difference can be seen when the pyrolysis temperature increased from 400 to 500°C (figure 5.11). Char yield production decreased from 62.2% to 48.5% while liquid and gas yield production increased from 7.1% to 22.3% for liquid and from 4.4% to 7.2% for gas yield. Due to the limited time provided as a visiting researcher at TU Delft, the Netherlands, only the yield product of gas has been analysed.

5.5.3 Gas yield production

The gas yields of the fast pyrolysis process at three different temperature settings were analysed using Micro GC. In this study, the gas compounds of the yield product identified were only the major compounds such as (CO_2), carbon monoxide (CO), hydrogen (H_2), nitrogen (N_2), and methane (CH_4). Using the software from Micro GC, the volume of each gas yield fraction was identified. The volume was later used to calculate the weight percentage of each fraction. As Nitrogen was used as the inert gas in this pyrolysis process, the gas yield identification result was normalised by not including Nitrogen, in order to avoid reading error and dilution effects [18].

Similar to the slow and intermediate pyrolysis processes, the fast pyrolysis of biomass that contained lignocellulose material produced gas dominated by CO_2 and CO. However, in contrast with the gas yield production from slow and intermediate pyrolysis processes, CO_2 and CO fractions increased as the pyrolysis temperature escalated. Since the char yield production decreased at the high temperature, it can be concluded that in fast pyrolysis, more of the feedstock's carbon elements are converted into syngas [18], [102].

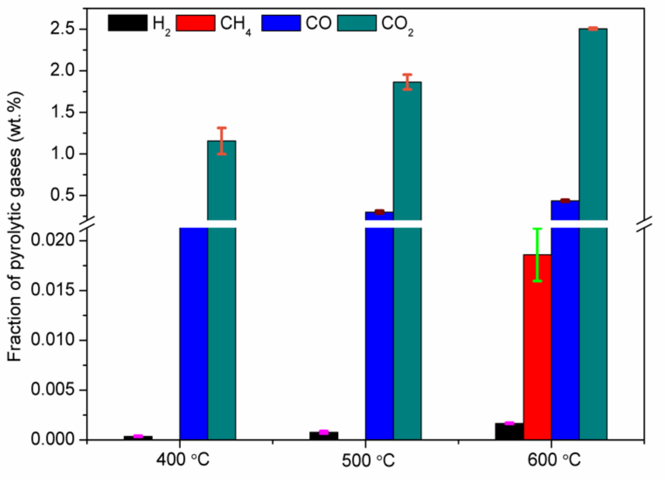

Figure 5.12 Fraction of pyrolysis gases in the pyroprobe, hydrogen (H_2), methane (CH_4) carbon monoxide (CO) and carbon dioxide (CO2).

As in TGA analysis, hemicellulose and cellulose are decomposed at the beginning of the heating process. As the temperature elevated, lignin was decomposed. As seen in figure 5.12, at the pyrolysis temperature between 400 and 500°C, the decomposition of hemicellulose and cellulose occurred as only the fraction of CO_2 and CO could be seen (very low H_2). Meanwhile, the decomposition of lignin was seen at the pyrolysis temperature of 600°C with the appearance of CH_4 fraction and the higher production of CO and H_2 [18].

The existence of methane and higher production of hydrogen at the pyrolysis temperature of 600°C is caused by the lignin decomposition process. In addition, it may also be caused by some oil yield evaporating into syngas. According to some research, the heavy hydrocarbon in the liquid yield would start evaporating (oil cracking) at a high temperature. The indication of this process is when the number of carbon monoxide and hydrogen fractions start to increase [18], [112].

5.5.4 Liquid yield production

The schematic diagram of fast pyrolysis equipment is shown in figure 5.13a. Vapour that produced during the fast pyrolysis process was condensed and trapped in a trap tube. The trap tube (figure 5.13b) was then measured using weight scale to obtain the mass of liquid yield (by subtracting the mass of trap tube after and before experiments). The pattern of the liquid yield fraction is shown in figure 5.11, which increased as a result of the escalating pyrolysis temperature. Prior to the identification analysis, oil (liquid yield) in trap tube was extracted and diluted using isopropanol. However, the similar case to the char yield analysis, the identification of liquid yield was not able due to the time limitation of the project in TU Delft.

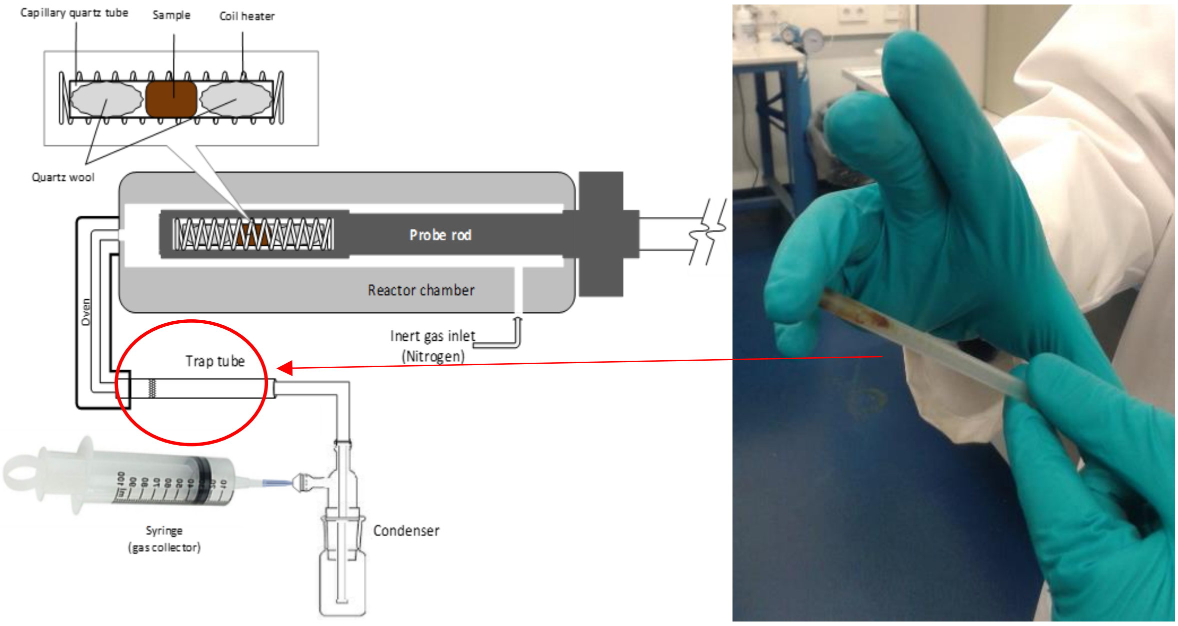

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Figure 5.13 (a) Schematic diagram of the pyroprobe, (b) trap tube

5.6 Mineral Content Analysis

The ultimate analysis data show that chicken litter has a considerably high content of ash, which can reach 30% of the chicken litter's dry weight. This indicates that chicken litter has a high non-volatile mineral content, which is advantageous, if the mineral content can be identified. The mineral content (per kg dry sample) of chicken litter can be identified using the Inductively Coupled Plasma (ICP) technique. Table 5.9 shows the identified mineral composition; the chicken litter contains a significant amount of phosphorus (P) and potassium (K). Therefore, chicken litter has high potential for use as fertiliser [18]. Base on the ICP data, the amount of P and K in PCL is higher than that of FCL. Consequently, PCL offers more value as a fertiliser.

Table 5.9 Element composition from chicken litter: Fresh Chicken Litter (FCL) and Pelletized Chicken Litter (PCL).

Element composition [mg/kg ash $_{\text{dry basis}}$]					
Major element			Minor element		
	FCL	PCL		FCL	PCL
Aluminum (Al)	1009.09	7302.21	Arsenic (As)	14.35	4.91
Calcium (Ca)	50765.18	110466.83	Barium (Ba)	210.43	226.04
Iron (Fe)	3835.49	13267.81	Cadmium (Cd)	4.78	0.00
Potassium (K)	258407.46	222142.51	Cobalt (Co)	9.56	4.91
Magnesium (Mg)	45552.37	57886.98	Chromium (Cr)	19.13	108.11
Sodium (Na)	32352.94	36555.28	Mercury (Hg)	4.78	14.74
phosphorus (P)	107771.40	84437.35	Molybdenum (Mo)	100.43	34.40
Sulfur (S)	31472.98	39739.56	Nickel (Ni)	47.82	142.51
Silicon (Si)	50172.17	81621.62	Lead (Pb)	23.91	44.23
Copper (Cu)	951.70	815.72	Antimony (Sb)	28.69	34.40
Manganese (Mn)	4662.84	5110.57	Selenium (Se)	9.56	24.57
Titanium (Ti)	124.34	766.58	Tin (Sn)	47.82	29.48
Zinc (Zn)	4414.16	3975.43	Vanadium (V)	33.48	29.48

When chicken litter is pyrolyzed, the mineral elements are accumulated in the char yield. As seen in Table 5.10, the mineral composition of each char is different, depending on the pyrolysis temperature. Compared to chicken litter, the mineral content (per kg dry sample) of char increases remarkably with temperature. This is because the pyrolysis process has a concentrated effect on char whereas in chicken litter, most of the volatile component is converted into liquid or gas yield [53][31]. The amount of P and K in char shows its potential for use as fertiliser. The Ni content in PCL is known to exceed the limit of 24 mg/kg $_{\text{dry sample}}$, which prevents its use for fertiliser [53][138][139]. Therefore, only the char produced from the FCL pyrolysis process has potential to be used as fertiliser.

Table 5. 10 Element composition from pyrolysis char generated from Fresh Chicken Litter (FCL) and Pelletized Chicken Litter (PCL) at 500, 600 and 700°C.

Element	**FCL** **mg/kg dry matter char**			**PCL** **mg/kg dry matter char**			**Poultry Litter Protocol**
	500°C	**600**°C	**700**°C	**500**°C	**600**°C	**700**°C	
Al	520.02	497.36	678.18	2604.42	2832.20	3456.99	
Ca	17628.47	22420.44	30054.34	37830.49	40260.57	45147.91	
Fe	1379.33	1437.38	1704.46	3952.82	4834.84	4503.85	
K	79444.66	86130.19	93609.82	75577.02	76206.71	38136.27	
Mg	9430.18	12545.06	17908.51	19963.90	21749.05	24886.43	
Na	10316.44	11403.35	12872.70	12436.09	12338.72	14167.80	
P	34729.00	35729.48	40365.85	29002.98	29024.50	32733.99	
S	9078.21	9022.53	9169.79	11198.52	11287.59	12683.45	
Si	15640.33	16007.77	18651.62	27884.64	28315.16	34665.61	
Ag	1.59	10.25	5.41	1.68	1.72	0.00	
As	7.93	3.42	1.80	1.68	0.00	3.91	17
Ba	57.08	73.49	88.38	78.92	85.88	113.28	
Cd	1.59	0.00	0.00	1.68	0.00	0.00	3
Co	3.17	3.42	3.61	1.68	1.72	3.91	11
Cr	7.93	8.55	9.02	41.98	39.50	46.87	31
Cu	331.36	326.44	371.55	273.71	278.24	320.31	596
Hg	3.17	1.71	3.61	0.00	1.72	1.95	0.5
Mn	1544.22	1563.86	1771.19	1717.81	1727.83	1962.87	3500
Mo	33.29	34.18	37.88	11.75	12.02	13.67	45
Ni	17.44	17.09	21.64	48.70	49.81	58.59	24
Pb	4.76	6.84	7.21	11.75	6.87	5.86	244

Sb	9.51	11.96	3.61	6.72	15.46	9.77	
Se	11.10	10.25	1.80	8.40	8.59	1.95	11
Ti	41.22	44.44	45.09	250.20	250.76	341.79	
Sn	3.17	3.42	32.47	60.45	27.48	15.62	
V	9.51	10.25	12.63	10.08	10.31	11.72	20
Zn	1407.87	1521.13	1585.41	1366.86	1367.15	1332.02	2063

5.7 Summary

A pyrolysis experiment using chicken litter as the feedstock was completed using slow, intermediate and fast pyrolysis. Before the pyrolysis process was conducted, the characteristics of the feedstock were identified. A significant amount of information can be obtained from the chicken litter characteristics and can be used to decide which pyrolysis method is most suitable to obtain the best result. As an example, for more liquid yield, feedstock that contains high volatile matter is ideal. For more char yield, feedstock with high fixed carbon is suitable.

The three pyrolysis methods used resulted in various yield products. In slow pyrolysis, the dominant yield product was char yield, particularly when the pyrolysis was performed at a low temperature. The intermediate pyrolysis process at the temperature of 500°C (as used in this study) resulted in the highest liquid yield. To obtain a high production of syngas, however, fast pyrolysis is the best option, especially at a high pyrolysis temperature. Since liquid yield generates a high caloric value, the intermediate pyrolysis will be focused upon for the simulation study.

Identification of the amount of mineral content in chicken litter and char demonstrates the high potential chicken litter has to be used as fertiliser. The mineral concentration in pyrolyzed char is even shown to increase with pyrolysis temperature. Therefore, it is reasonable to say that the pyrolysis process of chicken litter offers benefits. It can be used as an alternative energy source and the pyrolysis output can also be used for soil amelioration.

CHAPTER 6 Modelling and Economic Analysis of a Pyrolysis/ORC Power System

6.1 Introduction

The modelling reported in this chapter was developed using Aspen Plus™ software, to represent the pyrolysis process of chicken litter. This modelling technique allows the pyrolysis process to be simulated through the application of relevant parameters, from the completed experiments: working temperature, working pressure, feedstock characteristics and pyrolysis yield. The result of the simulation can be used to optimise the pyrolysis process of chicken litter to produce the maximum output. At these conditions the capacity of the system can be adjusted, to match the litter production of chicken farming in Indonesia.

The results from the pyrolysis were then used to simulate the energy conversion system and using the energy production of the system an economic analysis was performed.

6.2 Aspen Plus™ Modelling

Chicken litter pyrolysis generates three product yields: gas, liquid and char [16], [114]. Each product yield resulting from pyrolysis has a calorific value that can be used as an alternative energy source [140]–[142]. Gas yield needs to go through a gas purification process before it can be used as fuel for gas turbines, because gas turbines comprise of components that are highly sensitive to corrosion [143]–[145]. Through a combustion process, the elements in char product can generate energy. Moreover, they can also be used as soil ameliorant [18], [146]. The liquid yield of pyrolysis, which can also be used as fuel, has the benefits of easy storage and distribution because of its density. Of the three product yields, liquid yield has the highest calorific value [147], [148].

Based on the known benefits of liquid yield (easy storage and distribution), and its high calorific value, the model used in this simulation is the chicken litter pyrolysis that generates the highest liquid yield, namely the FCL pyrolysis at the pyrolysis temperature of 500°C. In general, the modelling is divided into two systems: the pyrolysis system modelling and the utilisation system modelling. Figure 6.1 shows that the liquid resulting from chicken litter pyrolysis is burned by combustion in an oil burner. The liquid yield can not be used for biodiesel engine (generator) because the liquid compounds have some acid molecules (corrosive). The heat of the oil burner is then used as the main energy source by the Organic Rankine Cycle (ORC) system, to generate electrical energy.

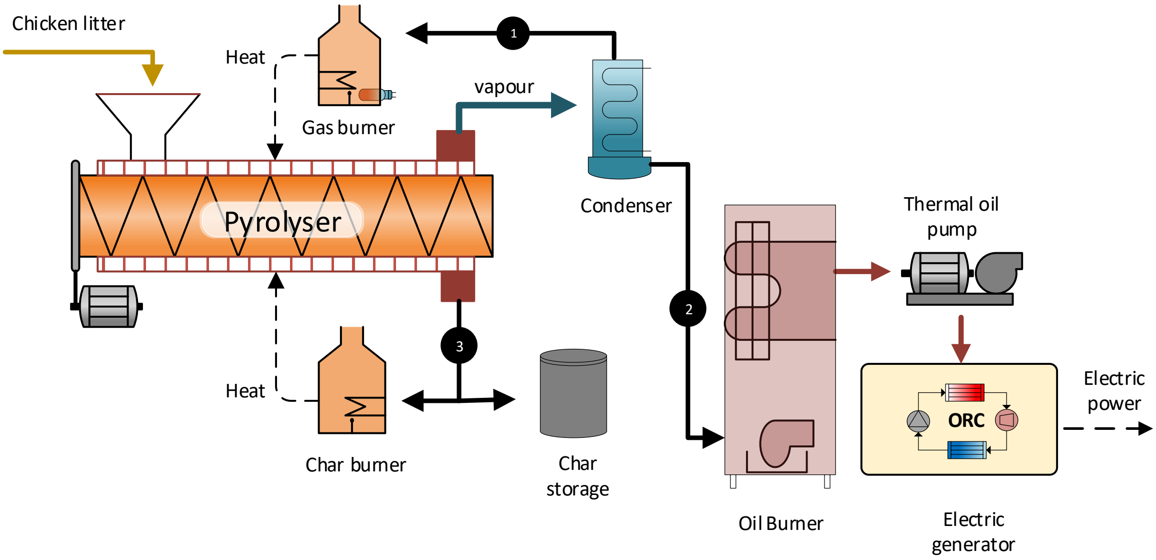

Figure 6. 1 Schematic diagram of utilisation of chicken litter pyrolysis, (1) gas yield, (2) liquid yield, (3) char yield.

6.2.1 Pyrolysis Simulation

The pyrolysis simulation with Aspen Plus™ is designed to use the equilibrium model approach, in which the data obtained from an experiment [149] is used for the working parameters and the result of the pyrolysis reaction. The experiment selected for the simulation model was the intermediate pyrolysis experiment at 500°C, using FCL as the feedstock. The selection of the model was based on the FCL pyrolysis experiment, which generated the highest liquid yield, at 500°C [150], [151]. Liquid yield can be more easily handled and transported, compared to gas and char yield. When liquid yield is used as an alternative energy source, even in a smaller volume, liquid yield generates a high energy value [152].

The production of chicken litter is based on chicken farming in Indonesia. Large scale chicken farming can produce as many as 400,000 chickens per batch [153], and the production of one batch takes approximately 30 to 32 days [154]. The amount of litter production from each chicken varies between 0.843–5.7 kg/bird/batch [155], [156]. The average value used for the simulation is 3kg/bird/batch. Assuming that farm cleaning is conducted every sixth batch [157], [158] and that one batch takes 30 days to produce, then the production rate of the chicken litter would be 40,000 kg/day (0.463 kg/s). This amount of chicken litter production (0.463 kg/s) is used as the flow stream input to the Aspen Plus™ simulation.

Since a chicken litter properties are not included in the list of Aspen Plus™ properties, it is categorized into the nonconventional type and identification is based on the proximate and ultimate analyses [159]. As displayed in Figure 6.2, chicken litter (CL) is decomposed into a conventional component in the block yield. The pyrolysis process in Figure 6.2 is represented by several blocks, namely H1 and PYRO. The PYRO block uses an RGIBBS equilibrium reactor, in which the pyrolysis reaction occurs at 500°C [149], [160]. The result of the reaction occurring in the PYRO block is based on the result of the FCL pyrolysis experiment at 500°C. The product resulting from the PYRO block is separated into hot vapour and char (CHAR-Y), based on the assumption that the char yield is solid carbon and ash element. The hot vapour is later cooled in the condenser (COND1) until the liquid product (LIQ-Y) and gas yield (GAS-Y) are generated.

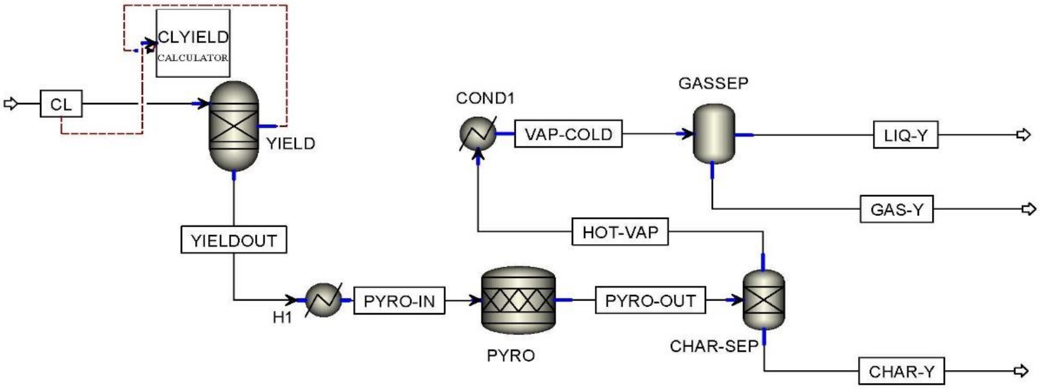

Figure 6.2 Chicken Litter (CL) Pyrolysis in Aspen Plus™.

Similar to the pyrolysis system proposed by Bridgewater and Yang, the chicken litter pyrolysis simulation uses the energy from char and syngas as the heat source [148], [161]. The energy required for pyrolysis is generated from burning all the gas yield and 35% of the char yield in the combustor, this can be seen in figure 6.3 that all gas yield and some char yield goes to the combustion process (in C-BURN block). The heat generated from the combustor is then used to satisfy the heat demand of the pyrolysis system.

Since all the gas yield is used in the combustion system, the end product generated from the chicken litter pyrolysis modelling is the 65% char yield (the 35% char yield was burned together with gas yield) and liquid yield. Char yield contains minerals with potential for soil amendment or fertilizer [65]. Liquid yield, with its high calorific value, can be used for conversion into electrical energy [142], [162], [163].

Considering the possible outcomes for the conversing chicken litter into useful resources, some scenarios are done as follow:

1. Mixture conversion.
2. All electricity conversion.
3. All fertilizer conversion.

The first scenario (mixture conversion) is converting all liquid yield into electric energy and selling the rest char yield (65%) as a soil amendment (fertiliser). The second scenario is converting all liquid yield and 65% char yield into electric energy. The first and the second scenario use the energy from all gas yield and 35 % char yield to satisfy the energy required of pyrolysis proses. Different from the first and second scenario, in the third scenario, the energy required for pyrolysis is satisfied by using all gas and liquid yield, and the char yield will be sold as fertiliser. The first scenario then simulated as shown in sub-chapter 6.2.2 below.

6.2.2 Utilisation Simulation

As shown in the schematic diagram (Figure 6.1), the liquid yield from the chicken litter pyrolysis is processed for combustion in the oil burner [164]–[166]. The heat generated from the oil burner is then used as the main energy source for an electric power generator. The electric generator selected for this simulation is the ORC [161], [167], based on its reliability and because the system only requires low to medium temperature heat to operate. The working fluid ORC boils at a temperature below the boiling point of water. The heat from the oil burner may reach 900°C. Therefore, a thermal oil cycle needs to be added to serve as the heat transfer fluid as well as the protector of fluid in the ORC, to prevent it from overheating [168]–[170]. Figure 6.3 shows the cycle of the chicken litter pyrolysis utilisation for power generation.

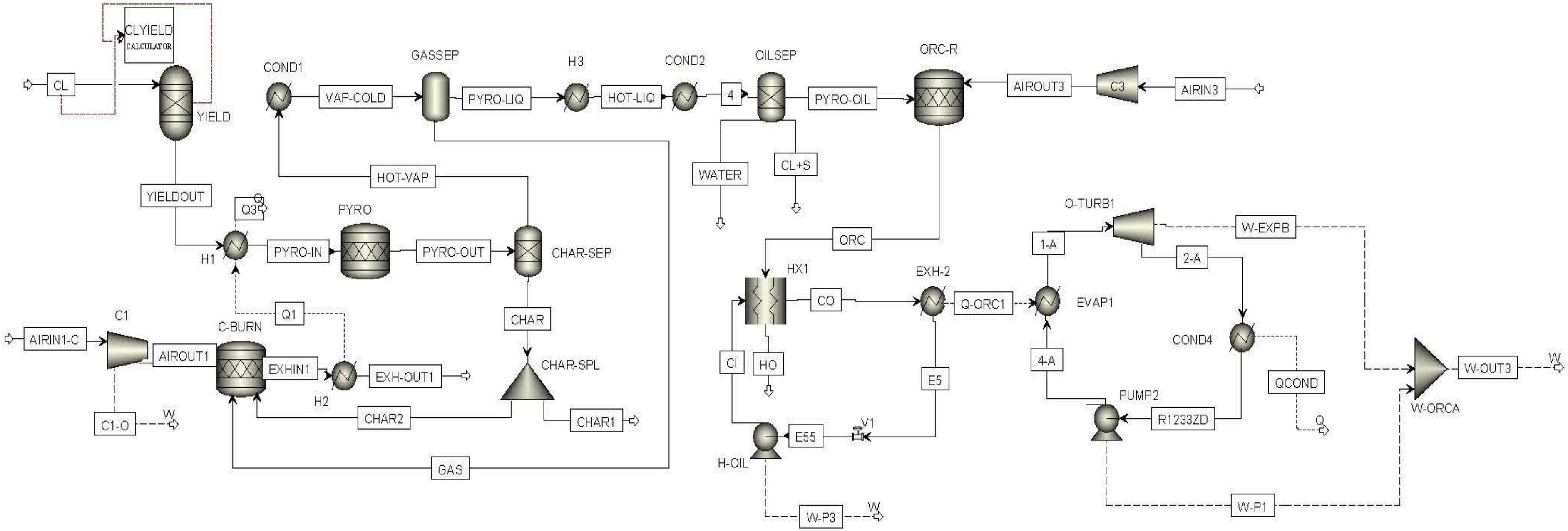

Figure 6. 3 Chicken Litter Pyrolysis Utilisation in Aspen Plus™.

ORC is a simple Rankine cycle that uses organic compounds instead of steam for its working fluid [171]–[173]. Careful selection of working fluid is important for the ORC because it affects the ORC engine performance [171]–[173]. For this simulation, R1233ZD is selected as the ORC working fluid. Compared to R245fa, R1233ZD has better thermodynamic properties. Furthermore, it is also environmentally-friendly as it is non-flammable, has a zero ozone depletion potential (ODP) and a low global warming potential of 1.0 [174]–[176].

Several researchers of small scale ORCs point out that the isentropic efficiency of an ORC's expander ranges from 50 to 80% with the expansion ratio between 5–10 [177]–[179]. For the ORC simulation, the turbine used as the expander was set to have an efficiency of 50%, with the pressure drop of 21 bar. Table 6.1 shows the data obtained from the simulation of the ORC system. The energy input used by the ORC system came from the thermal oil that was transferred from the oil burner. By comparing the energy input and the electrical energy (as the energy output), the overall efficiency of the ORC was determined to be 6.5%.

Table 6. 1 ORC Property.

Item	Data (from simulation)
Evaporator Temperature	151°C
Evaporator Pressure	31 bar
Condenser Temperature	30°C
Condenser Pressure	1.48 bar
Fuel rate (liquid yield)	0.21 kg/s
Overall Efficiency	6.5 %
Electric Power	151 kWe

6.3 Economic evaluation

An economic evaluation was performed to explore the feasibility of running the project. Two methods that can be used to perform an economic evaluation are the payback period and the net present value (NPV). The payback period (PP) method aims to identify how long it would take for an investment to be reimbursed. The NPV method aims to determine the profit value within a certain period of time [180]–[183].

6.3.1 Pyrolysis Cost

Bridgewater compiled an economic analysis of a number of pyrolysis and gasification system experiments. Using up-to-date data from the year 2000, Bridgewater developed an equation to obtain the value of the total pyrolysis plant. The equation was developed by making a regression of 14 data values for the pyrolysis cost module [148]. The study used the following equation to calculate the cost of constructing a pyrolysis system.

$$TPC_P = 40.8 \times (Q_h \times 1000)^{0.619} \quad \text{……………………………………………………….. 6.1}$$

Where,

TPC_P = Total plant cost of pyrolysis reactor system, k€

Q_h = Mass flow rate of dry feedstock, tonne/h

From the pyrolysis simulation, the mass flowrate of the used feedstock was 0.463 kg/s or 1.67 tonnes/h. Assuming that the moisture content of the chicken litter used as feedstock was 22.67%, then the mass flow rate of the dry feedstock would be 1.29 tonnes/h. Using equation 6.1, the cost of developing a pyrolysis system would be €3,446.35k.

The simulation of the chicken litter pyrolysis process aims to maximise the liquid yield product. When the pyrolysis process is not in operation, a buffer tank is required to store the liquid yield, to allow continuity of liquid yield supply. In addition to the buffer tank, a transfer pump is also required to ensure the circulation of the liquid in the system. Equation 6.2 calculates the total plant cost of the buffer tank system used in the pyrolysis process [148].

$$TPC_S = 119 \times (Q_{Liq})^{0.4045} \quad \text{……….…………………………………………………….. 6.2}$$

Where,

TPC_S = Total plant cost of liquid storage system, k€

Q_{Liq} = Liquid yield flow rate, tonne/h

The chicken litter used in the simulation is the FCL with a pyrolysis temperature of 500°C. In the pyrolysis experiment using the FCL as feedstock, a liquid yield fraction of 57.8% was obtained. The mass flow of the feedstock used for the simulation was 0.463 kg/s, and therefore, a liquid yield of 0.268 kg/s or 0.96 tonnes/h was obtained. Using equation 6.2, the total plant cost for the liquid storage equalled €117.22k. Assuming that the pyrolysis process is performed within the locality of the source chicken farm, the transportation cost can be neglected. Therefore, the total cost for the pyrolysis system would be the total of the pyrolysis plant reactor and liquid storage, which amounts to €3,563.57k. However, this result was based on Bridgewater's two equations (equations 6.1 and 6.2) which were valid for the year 2000.

If the total plant cost (TPC_P and TPC_S) is equal to the component price, then the cost value needs to be corrected. To correct the cost for the year 2019, the inflation rate between 2000 and 2019 was used. The statistical office of the European Union (Eurostat) reports that the European Union's annual inflation in July 2019 was 1.4 % and 2.2% in the previous year [184]. Assuming that the average inflation rate is 1.8% annually (using the average from years 2018 and 2019), then the total inflation between 2000 and 2019 can be estimated to be 34.2% (19 × 1.8%).

The total inflation between 2000 and 2019 (43.2%) was then used to revise the total cost of the pyrolysis system, which increased from €3,563.57k to €4,782.31k. The resulting value is in line with a calculation performed by Peacocke [162]. Peacocke compared two pyrolysis systems of two companies (Welman and BTG). The comparison shows that the capital cost of pyrolysis increases with the capacity (Figure 6.4).

Alan McDonald and Leo Schrattenholzer introduce a learning curves for the cost of the improvement of technology in energy conversion. They suggested the learning rate is 0.15 for the use of electricity from biomass technology [195], which means, the capital cost will reduce by 15% after the first technology was initially applied. However, by considering the worst-case scenario, the learning rate is not used in the calculation of pyrolysis installation cost.

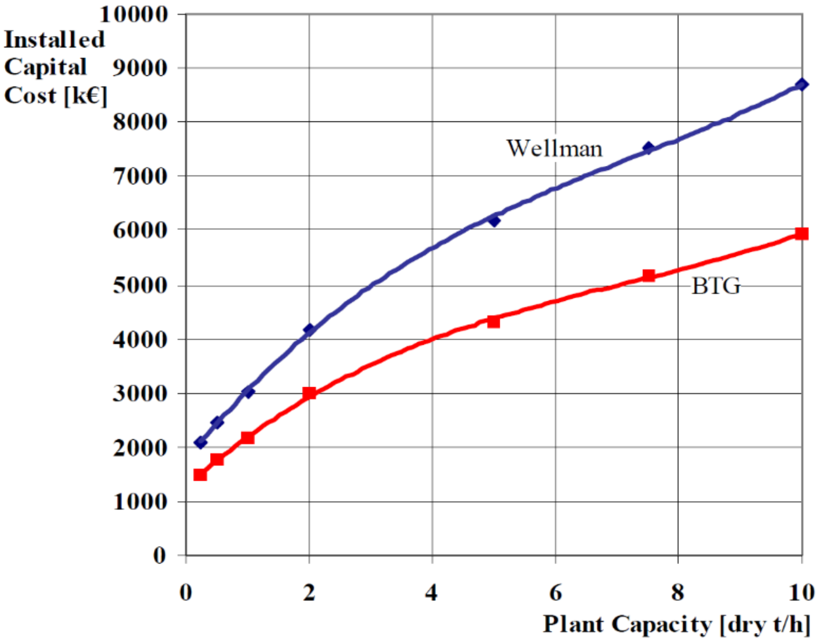

Figure 6.4 Capital cost for pyrolysis process installation for two companies, Wellman and BTG. [162].

6.3.2 ORC Investment

Presently, the small-capacity ORC system (1–100 kW) is expensive and not widely available for purchase. For this reason, it is not competitive compared to the other established technologies that utilise renewable energy. Aiming to increase the competitiveness of the ORC cost, Tocci shows average costs from available technologies, which include solar photovoltaic, wind, hydro, gas turbine and the internal combustion engine (ICE). Tocci then approximated a trend line to estimate costs of the ORC. Figure 6.5 shows that ORC cost with a capacity of 10–100 kW cannot exceed 2500 €/kW [162].

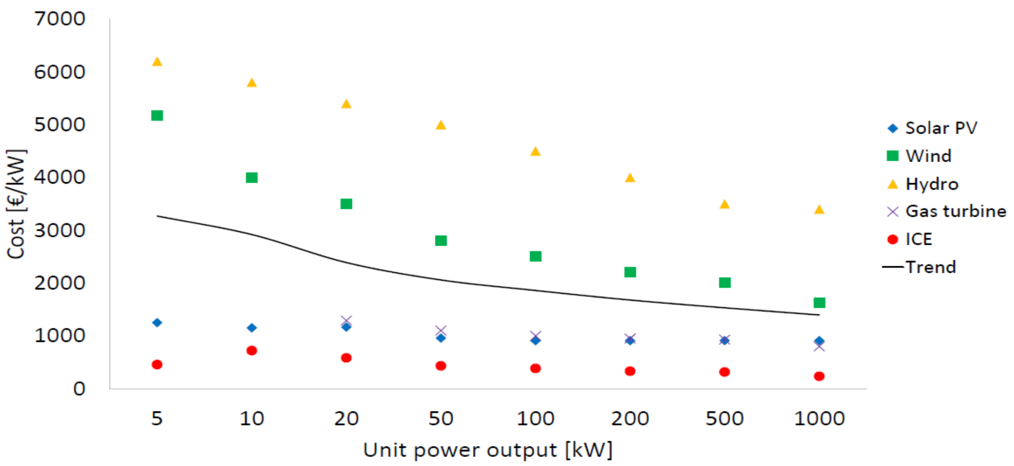

Figure 6.5 Costs versus power output for energy technologies and estimate for ORC (Trend) [27]. (ICE, Internal Combustion Engine).

Different from Tocci, Tchance performed an estimation by comparing ORC cost from a reference cost, using equation 6.3 [182]. The ORC system used as reference had a capacity of 2 kW with a specific cost of 5,775 €/kW.

$$C_S = C_{S,ref} \times (W_{net} / W_{net,ref})^{0.8} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; 6.3$$

Where,

C_S = Specific ORC cost, €/kW

$C_{S,ref}$ = ORC specific cost reference (5,775 €/kW)

W_{net} = ORC capacity to be installed, kW

$W_{net,ref}$ = 2 kW (ORC capacity reference)

Using equation 6.3, the specific ORC cost of the simulated ORC system is:

$$C_S = 5{,}775 \times (151/\ 2)^{0.8}$$
$$= 18{,}3615.6 \text{ €/kW}$$

The estimated value of the specific ORC cost obtained using equation 6.3 is higher than the estimation performed by Tocci, which is 2,500 €/kW (for the year 2017), which is similar to the specific ORC cost published by Leme, whose calculation for an ORC capacity of 2230 kW, resulted in a specific cost of 3,516 $/kW (for the year 2018) [185]. Assuming that for 2018, the exchange rate for Euros to US dollars was 0.81 on average, then Leme’s specific cost would be 2,848 €/kW.

Acknowledging the slightly different specific ORC costs published by Leme and Tocci, this study selected Tocci's estimation method of 2,500 €/kW. As a result, the installed cost of the ORC system used in this simulation is €377,500. If the installed cost of ORC is equal to the equipment price, then the inflation rate needs to be considered. The total inflation rate from year 2017 to 2019 is assumed to be 3.6% (from an average of 1.8% per year), then the ORC installed cost would be €391,090.

The initial investment value is calculated from the total installation costs of the pyrolysis and ORC system, which is €4,782,310.00 + €391,090.00 = **€5,173,400.00**. If the Indonesian to Euros currency exchange rate is IDR14,989.9 for €1 (www.oanda.com, July 2019), the initial investment required would be **71,682,044,590.00 + 5,862,399,991.00 =IDR77,544,444,440.00**

6.3.3 Variable Cost

The installation cost of the pyrolysis and ORC system is the initial cost that makes up the initial investment value of the project. The purpose of the pyrolysis and ORC system installation is for electricity generation. As a consequence, when the electric generation is running, a routine running cost will also be expended, for maintenance and utility costs, for example. Even when the electricity generation system is not working, there will be a cost, namely the labour cost.

a. Labour Cost

To obtain an optimum benefit, the system needs to operate 24 hours a day. For one operational day, the working hours are divided into 3 shifts. Each shift has 1 supervisor and 4 operators. For daily managerial duties, 1 general manager, 1 technical manager and 1 administrator are in charge [162], [186]. The total number of workers needed is 18. The following is the labour cost calculation, obtained using the Indonesian standard monthly wage (using the Indonesian currency, IDR) in accordance with the regulation from the Ministry of Manpower [56]:

General manager : IDR 20,000,000.00 × 1 = IDR 20,000,000.00
Technical manager : IDR 8,000,000.00 × 1 = IDR 8,000,000.00
Administrator : IDR 4,000,000.00 × 1 = IDR 4,000,000.00
Supervisor : IDR 4,000,000.00 × 3 = IDR 12,000,000.00
Operator : IDR 2,500,000.00 × 12 = IDR 30,000,000.00
Total = **IDR 74,000,000.00** (monthly)

b. Utility Cost

Utilities are necessary to support the operational plant and office/laboratory, which also consume electricity and water. For this study, the electricity and water are supplied by the state-owned enterprise. The purpose is to ensure the continuity of supply during the process of electricity generation. From the literature, daily electricity consumption is 28 kWh for each wet feedstock, while the water consumption is 13 m^3 (including the sewerage surcharge) for daily and each wet feedstock [187].

If the wet feedstock (FCL) is the one used in the simulation process, then the electricity consumption will be 46.76 kW and the water consumption will be 21.71.m^3. The following are the utility costs obtained by assuming that the system operates 24 hours a day (720 hours/month), using the electricity and water tariff applied to Indonesian industrial sectors [188], [189]:

Electricity bill: 46.76 × 720 × IDR 1,112.00 = IDR 37,437,926.40
Water bill : 21.71 × 720 × IDR12,550.00 = IDR 196,171,560.00
Total = **IDR 233,609,486.40** (monthly)

c. Maintenance and Overhead Cost

The maintenance and overheads calculation is based on annual costs. This is calculated from a percentage of the pyrolysis and ORC system installation cost, which is assumed to be 2.5% for maintenance and 2% for overheads costs. As a result, the total for maintenance and overhead costs is [187]:

Maintenance cost : 2.5% × €5,173,400.00/12 = €10,777.92
Overhead cost : 2% × €5,173,400.00/12 = €8,622.33
Total = **€ 19,400.25** (monthly)
= **IDR 290,808,000.00** (monthly)

The total for labour, utility, maintenance and overhead costs is the monthly operational cost for the electricity generation process, which is:

74,000,000.00 + 233,609,486.40 + 290,808,000.00 **= IDR 598,417,486.40**

6.3.4 Income

To accelerate the development of renewable energy-based technology, the Indonesian Government provides an incentive in the form of a 30% tax income reduction for enterprises in the sector of renewable energy technology. Unfortunately, the incentive does not apply to technology that converts energy from biomass waste [190]. The same applies for the gate fee or tipping fee from local governments, which is given only to enterprises that process domestic waste / municipal solid waste (MSW), under a specific condition that the waste is processed into electric energy [191].

In 2020, through the Indonesian presidential regulation, a feed-in tariff was introduced to boost investment in the field of renewable energy. The feed-in tariff applies only for technologies based on hydro-, solar- and wind power [192]. In the absence of an incentive and an additional tariff from the government, an income from the chicken litter pyrolysis and ORC system can only be generated from the sale of the electricity generated. In order to gain an optimum advantage, the system needs to run 24 hours a day with 100% of the electrical energy produced sold to industry.

If the unit price of electricity is IDR 1,112.00/kWh, then the amount of the monthly electrical energy sold will be as follows:

Electric output from ORC : 151 kWe
Electricity sale : 151 × 720 × IDR 1,112.00 = **IDR 120,896,640.00**

Indonesia has a tropical climate. As a result, the excess heat of the ORC condenser has no economic value. However, the 65% of the char left as a result of pyrolysis can be used as fertilizer. The char yield fraction of the FCL pyrolysis process is 35.8% of the wet feedstock's weight. If the flow rate of the feedstock is 0.463 kg/s, the amount of char that could be generated in one month (30 days) is 279 tonnes. The average fertilizer price on the Indonesian market is IDR 6,800.00/kg [193]. If the 65% of char yield is sold as fertilizer, the income generated would therefore be **IDR 1,897,200,000.00.** This would make the total income generated from the pyrolysis process amount to **IDR 2,018,096,640.00**.

Comparing the total income (IDR 2,018,096,640.00) to the monthly total running costs (IDR 598,417,486.4), a profit of **IDR 1,419,679,153.60** could be gained.

6.3.5 Carbon emission

In Indonesia, the electricity is mainly supplied by a government enterprise. Some of the electric grid are powered by renewable energy such as wind turbine, water turbine and geothermal turbine. However, since the technology of renewable energy is for long term implementation, then the conventional electric generator is keep operating. The energy for generators are greatly provided by coal which has the average carbon emission 0.867 kg CO_2/kWh [194].

Because chicken litter consists of natural bedding material, then chicken litter can be classified as biomass. The conversion of chicken litter into electric energy, then can be considered as carbon neutral process. Since the electric generation (151 kW) is carbon neutral, then the carbon emission that can be saved in a year is :

151 kW × 8640 × 0.867 kg CO_2/kWh = 1131122.8 kg CO_2 = **1131 tonnes CO_2**

6.3.6 The different scenario

The second scenario is converting all liquid yield and the rest char yield (65%) into electric energy. The conversion of liquid yield into electric energy has been done in the simulation at sub-chapter 6.2.2, and the calculation of the conversion char yield into electric energy follows the steps below:

- Char yield caloric value from table 5.4 is **19.31 MJ/kg**
- By using the yield fraction in figure 5.7 (char yield is 35.8%) and the feedstock flow rate in simulation, then the mass flow rate of char is: 65%×35.8% ×0.463= **0.11kg/s**
- Overall efficiency from table 6.1 is **6.5%.**

- Then the electricity produced from char is: 19.31×1000 ×0.11×6.5%= **138 kW**
- The **total** of electric energy in scenario 2 is:
  P_T = 151 + 138 = 289 kWe

If the unit price of electricity is IDR 1,112.00/kWh, then the monthly electrical energy sold carbon emission emission saving will be as follows:

Electricity sale: 289 × 720 × IDR 1,112.00 = **IDR 231,384,960.00**

CO_2 emission saving: 289×8640×0.867 = 2164864.3 kg CO_2 = **2165 tonnes CO_2**

The third scenario is using the char selling as the main income of the chicken litter conversion by pyrolysis process. If char yield fraction is 35.8% and the fertilizer price is IDR 6,800.00/kg, then the total char selling that can be generated in a month is:

35.8%×0.463kg/s×2592000s×IDR 6,800.00/kg = **IDR 2,921,513,702.00**

Since there is no pyrolysis product that converted into electric energy, the ORC cost (€391,090.00) can be eliminated. However, the variable cost is included for the pyrolysis process attribute. The result of the three scenarios is shown in table 6.2

Table 6. 2 Scenario of Chicken Litter conversion

	Cost (in million IDR)			Income (in million IDR)		CO2 emission saving (tonnes/year)
	Pyrolysis	**ORC**	**Variable**	**Electric**	**Fertilizer**	
Scenario 1	71682	5862	598.4	120	1897	1131
Scenario 2	71682	5862	598.4	231	-	2165
Scenario 3	71682	-	598.4	-	2922	-

Table 6.2 shows the comparison among the three scenario of chicken litter conversion. By selling both electric and fertilizer, scenario 1 give more positive value not only a revenue but also saving in CO_2 emission. The second scenario gives the highest saving of CO_2 emission. However, the income from the electric selling is lower than monthly variable cost, which means the scenario 2 would not be able to give a positive revenue. The highest income is coming from the third scenario and three times higher than the variable cost. The third scenario will give faster return in capital investment. However, there is no saving carbon emission in this scenario

and would not any positive impact to the environment. Since only scenario 1 gives positive impact for environment and a revenue, then the economic evaluation is done by using the scenario 1

6.3.7 Economic evaluation

The methods that can be used to perform an economic evaluation are PP and NPV. The equation 6.4 for PP can be used to discover how long it would take for an investment to reach its break-even point. The following is the monthly-based calculation [180]–[182].

PP = Initial investment/(Income-Operating cost) ……………………………………….. 6.4

Then:

PP = 77,548,800,000.00/(2,018,096,640.00-598,417,486.40)
= 54.62
= 55 months (4 years and 7 months)

The PP calculation shows that the investment will have a break even period of 4 years 7 months. However, if the initial investment is obtained through a bank loan, the economic analysis should also take into account interest and the inflation rate. The NPV method includes the interest of the loan and inflation rate. Equation 6.5 is then used [180], [182].

$$NPV = -C_i + \sum_{n=1}^{N} \frac{F_n}{(1+K)^n} \quad \text{………………………………………………………. 6.5}$$

Where,

C_i = Initial investment
n = time period
Fn = yearly cash flow (income-operating cost)
N = years of investment's life
K = discount rate (interest + inflation rate)

If the investment is funded by a bank loan with an annual interest rate of 12% and the Indonesian inflation rate is 3%, the annual discount rate will be 12%+3% = 15%. Assuming that the lifetime investment of the pyrolysis is 9 years (the longest period that gives positive NPV value), the NPV value will be [180]:

$$NPV = -77{,}548{,}800{,}000.00 + \sum_{n=1}^{9} \frac{1{,}419{,}679{,}153.60 \times 12}{(1 + 15\%)^{n}}$$

NPV = 3,740,618,645.96

The positive NPV value indicates the feasibility of the investment into the electricity generation system over a period of nine years.

6.4 Summary

A simulation for the pyrolysis process and electricity generation was performed using Aspen Plus™ software. The FCL pyrolysis process generates the liquid yield product which can be burned. The heat generated from the burning process can be used for the ORC system. With the overall efficiency of 6.5%, the ORC system from the simulation generates electric power output of 151 kW.

An economic evaluation was performed for both the pyrolysis and ORC system, using the economic conditions in Indonesia for the parameters. The analysis shows that the pyrolysis and ORC system have an economic value from char sale, that can be used as fertilizer. The sale of electricity and char can generate a monthly profit that reaches IDR 1,419,679,153.60. Finally, the result of the economic analysis of the NPV indicates a return on investment for the pyrolysis and ORC system investment within a period of nine years. This long return period is primarily due to the high interest rate charged by the banks in Indonesia and the lack of investment incentives from the government of Indonesia.

Chapter 7. Conclusions and Recommendations for Further Work

The consumption of chicken meat is increasing annually. The increase has motivated the chicken farming industry to raise their production capacity. As a consequence, chicken farming produces more waste. Without proper treatment, litter arising from chicken farming may cause problems to the environment, one of which is pollution. The forming of nitrate compounds for example, may be absorbed by the soil and pollute the ground water. Another example is the formation of ammonia, which evaporates and causes odour issues. Another method of utilizing chicken litter as a resource is its use to generate energy.

Several methods can be applied to convert chicken litter into useful energy, namely combustion, anaerobic digestion, pyrolysis and gasification. In this study, the method explored in detail is pyrolysis. Pyrolysis method is divided into three categories that include slow, intermediate and fast pyrolysis. The temperature of each of these pyrolysis methods was varied in an effort to investigate the effect of temperature on the bioproducts of the process.

In addition to the literature studies, the data presented in this study was obtained from experiments, simulation and economic analysis. The experimental work was conducted in three different locations. The slow pyrolysis experiment was performed at the laboratory of the RCUK Centre for Sustainable Energy Use in Food chains (CSEF), Brunel University London. The intermediate pyrolysis experiment was performed at a facility of the Department of Chemical Sciences, Bernal Institute, University of Limerick and the fast pyrolysis experiments was performed at the Process and Energy Laboratory, Delft University of Technology. The details of each work are as follows.

- Slow pyrolysis. The experiment work of slow pyrolysis was started by planning a pyrolysis experiment by using a pyrolysis test rig. Based on the literature study, a pyrolysis test rig was designed and developed. The construction of the test rig was started by a series of procuring processes including procuring the control equipment and the pyrolysis system components such as reactor, condenser and gas and liquid yield collector which was attached to the lab stand support. The control equipment was installed in the control box and was then connected to the heater that cover the pyrolysis reactor.

- Intermediate pyrolysis. Due to the limitation of facilities at Brunel University, such as elemental analyzer, bomb calorimeter, micro GC, GC MSD, the intermediate pyrolysis was performed at another facility that could support the experiment. The laboratory, which is part of the facility owned by the Department of Chemical Sciences, University of Limerick, had the required equipment to perform the experiments. All of the yield products of the slow and intermediate pyrolysis were also tested in this laboratory.

- Fast pyrolysis. For fast pyrolysis, the experiments were performed by using the 100yroprobe 5000 series, a required equipment that could be found at the Process and Energy Laboratory, Delft University of Technology. Access and funds to use the facility was obtained through the Transnational Access afforded through the BRISK2 program.

- Following the completion of the experiments, a simulation study using Aspen plus software was performed to investigate the feasibility of electrical energy generation using the heat from combustion of the products of pyrolysis. The simulation assumed that the Organic Rankine cycle (ORC) would be used for the power generation.

- The final phase of the study was focused on the economic evaluation, which was performed to investigate the feasibility of the chicken litter conversion to usable energy and fertilizer. The evaluation was performed by using financial parameters for Indonesia.

This chapter summarises the conclusions from the study and provides suggestions for further work.

7.1 Conclusions

1

In addition to its use as fertilizer or soil ameliorant, chicken litter can be converted into a useful energy source. The literature survey pointed to a number of methods for conversion of chicken litter to useful energy.

1. The Combustion method, which is a method of chicken litter burning. The energy generated from chicken litter combustion can reach 14.6 MJ/kg. This energy can be used for the generation of steam or heat up other fluids in a closed cycle heat to power system to generate electrical power.

2. Anaerobic digestion can be used for the degradation of chicken litter in the presence of bacteria. During the degradation process, methane gas, also known as biogas, will form. The calorific value of biogas ranges between 0.47-0.51 MJ/kg. This gas can then be combusted in a boiler to produced heat or in internal combustion engine based combined heat and power systems to generate electrical power.

3. Pyrolysis is the process of heating chicken litter at the temperature between 300-800°C, in the absence of oxygen. The main product of the process is char, gas and liquid (bio-oil). The calorific value of the liquid product could reach 29.6 MJ/kg.

4. Gasification is a process that takes place at the temperature between 800-1200°C and in air is added during the process. The product of the process is gas, also known as synthesis gas (syngas), with the caloric value that could reach 5.4 MJ/kg.

The combustion method for chicken litter is already mature with a number of commercial plants operating in some countries such as the US and UK. Meanwhile, the anaerobic digestion method is considered less effective due to the low level of moisture in chicken litter. In terms of the gasification process, since it takes place at a high temperature, high energy input is required in this method.

Pyrolysis process generated yield products that include gas (syngas), liquid (bio-oil) and char. Among the three yield products, liquid yield has the highest calorific value and therefore, the liquid yield as the result of chicken litter pyrolysis process delivered a potential to become biofuel and serve as an alternative energy source to replace fossil fuel. This study focused on the pyrolysis method as it offers the highest potential for energy production.

2 Because it is heterogeneous in nature, the chicken litter used as feedstock cannot be represented by only one type of sample. The following are several types of chicken litter used as feedstock in the experiments.

- Hay mix (chicken manure + hay),
- Straw mix (chicken manure + straw),
- Rice husk mix (chicken manure + rice husk),
- Wood shavings mix (chicken manure + wood shavings),
- Fresh chicken litter (FCL) and
- Pelletized chicken litter (PCL).

The characteristics of all types of chicken litter used for the experiments were investigated by applying the proximate analysis method (moisture, volatile matter, ash and fix carbon content) and ultimate analysis method (carbon, hydrogen, oxygen, nitrogen and sulphur content). The result of the chicken litter analysis conducted can be summarised as follows.

1. The high level of fix carbon found in rice husk mix means that it is likely that it would be the highest char producer in the pyrolysis process.

2. Liquid yield was the highest from the wood shavings mix that also has the highest level of volatile compounds.

3. The high carbon I element would indicate that PCL would have the highest caloric value in the combustion process.

4. Fresh chicken litter (FCL) had the highest moisture content compared to the other types of feedstock. It would indicate that the energy conversion process by using FCL would require more energy.

3 The investigation of pyrolysis process in this study was conducted by performing a series of experiments that applied three different methods of pyrolysis. Each set of experiments involved a different temperature setting and different type of chicken litter. The following are key outputs from the investigations.

1. The yield production from pyrolysis highly depends on the pyrolysis method as well as on the temperature setting of the pyrolysis reactor.

2. The slow pyrolysis resulted in more chars, compared to the other methods. The char production decreased as the pyrolysis temperature increased.

3. The liquid yield is the dominant product of intermediate pyrolysis, especially at low temperature.

4. Gas production is high in fast pyrolysis, especially at the highest temperature levels.

5. Fresh chicken litter (FCL) has a high level of moisture content (22.67 wt%) compared to PCL (4.84%). However, the liquid yield of both the FCL and PCL pyrolysis had high water content, which ranged between 70 – 80 wt%. This indicates that the chicken litter pyrolysis process will likely lead to liquid yields with high level of moisture content.

4 Aspen plus was used to simulate how the chicken litter pyrolysis process could generate electrical energy. In the simulation, the pyrolysis process was combined with an electric generator which was modelled by assuming that the heat to power systems would be based on the organic Rankine cycle (ORC) system. The simulation of the pyrolysis process used the data from the experiments that resulted in the highest liquid yield, which was from the FCL pyrolysis at the temperature of 500°C. The amount of chicken litter used in the simulation was taken based on the calculation of the chicken farming capacity in Indonesia, which was 400,000 chicken per batch. With the overall efficiency of 6.5%, the ORC system was estimated to be able to produce electric power of the order of 150 kWe.

5 In order to improve the confidence of using chicken litter as a resource for electrical power generator, an economic analysis was performed, by carrying out an economic analysis based on the simplified Payback Period and the Net Present Value (NPV) of the investment. The results of the evaluation are as follows:

1. The payback period was calculated as the time needed to return the initial investment, taking into account the initial investment, the operating cost of the system and the financial return from the sale or utilization of the energy produced and the sale of a biochar. Using financial parameters for Indonesia the basic payback period was estimated to be approximately 5 years.

2. Assuming that the initial investment was a bank loan and the interest that will be incurred and the inflation rate over the period, calculation of the NPV showed that the investment will start generating positive net income in approximately 9 years.

3. The above analysis only considers financial benefits. The system will also need to environmental as well as social benefits from the reduction of pollution and the generation of renewable electricity from waste which will displace fossil fuel generated electricity in central power stations. If the electricity generated is used on site, then the technology will be able to be used in remote areas with limited or no access to the electricity grid.

7.2 Recommendations for further work

The study focused on chicken litter conversion into usable energy using the pyrolysis method. The slow, intermediate and fast pyrolysis methods have been investigated through experimentation and modelling. Simulation results and economic analysis demonstrated that pyrolysis of chicken litter and the use of the products of pyrolysis as a fuel to drive Organic Rankine Systems can be feasible for distributed power generation. The biochar can be used as a biofertilizer and therefore it has an economic value. There is still considerable work to be done on the subject for the optimum design of energy production systems using chicken litter as the feedstock. Recommendations for further work include:

1. Chicken litter consists of materials that are not homogenous. As a consequence, each type has different characteristics. Future studies should consider chicken litter from the locality where consideration is given to its use for electrical power production. The use of chicken litter from Indonesia was not possible in this thesis but this is something that new research with regards to Indonesia should aim to do.
2. Due to a lack of appropriate energy measurement equipment, the energy input for chicken litter pyrolysis was not measured. The emphasis was more on the analysis of the characteristics of the outputs of the process. It would be ideal for future studies to measure the energy input during the pyrolysis process to ensure that more accurate inputs are included in the Aspen plus simulations.

3. To prevent errors during sample testing of the pyrolysis results, it is recommended to place the analysis equipment such as Micro GC and GC MSD in-line with the pyrolysis test rig so that the analysis is performed in real time. This would not only reduce the possibility of errors but would also make it more effective and time saving.

4. The use of the fuel produced by chicken litter pyrolysis to generate heat to drive the ORC system was analysed using Aspen plus simulation. In order to understand in detailed the behaviour of the system and validate simulation results, it would be useful to develop a prototype pyrolysis and ORC system integration to enable experimentation on the whole integrated system.

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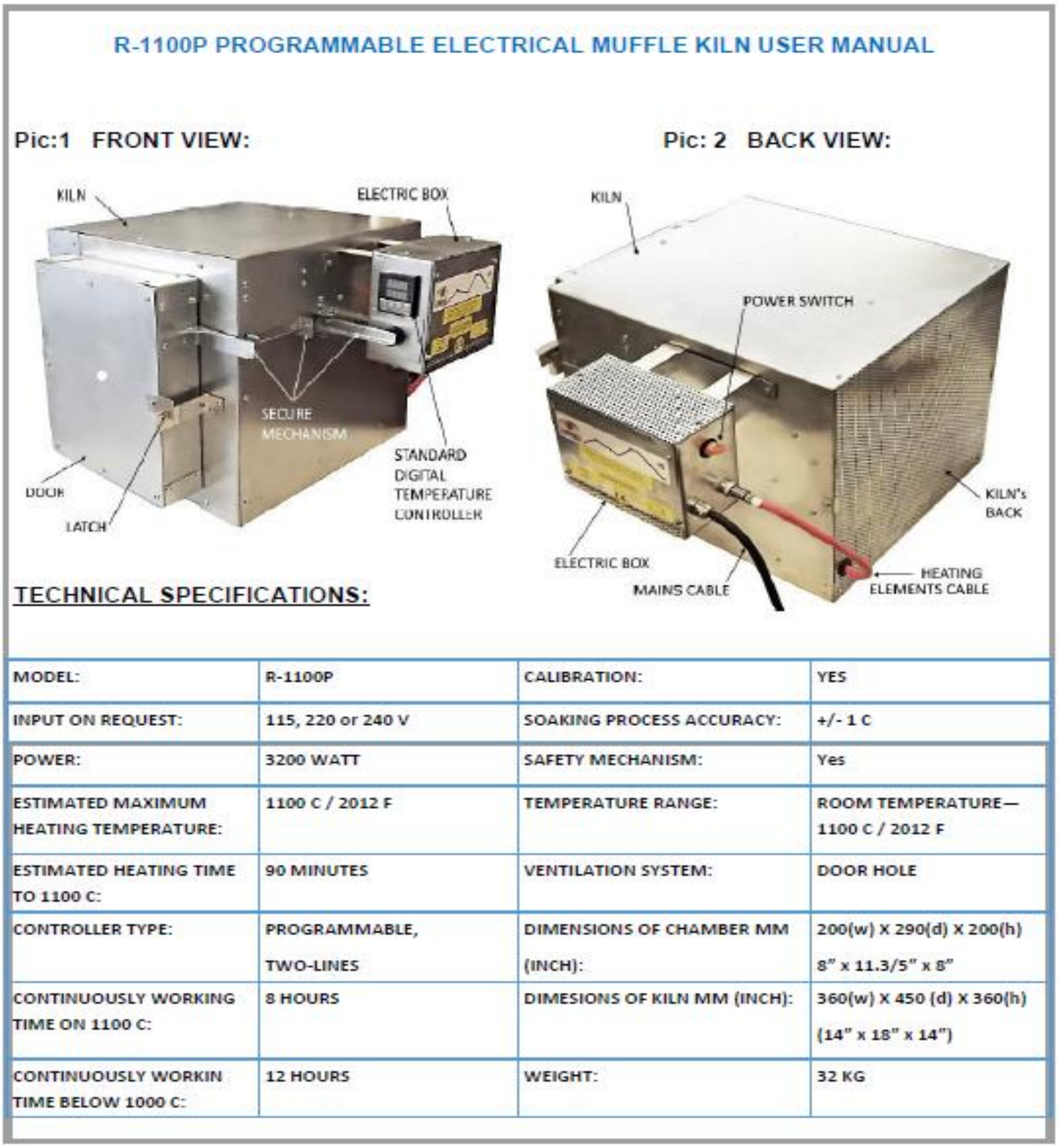
APPENDICES

Appendix A

Photographs and pictures of the equipment pieces used during the chicken litter pyrolysis experiments, as well as the activities conducted during the experiments at TU Delft, the Netherlands.

1. Pyrolysis equipment in CSEF, Brunel University London.

Fig. A.1 is a muffle kiln which was used for the proximate analysis of all samples prepared at Brunel University that included hay mix, straw mix, wood shavings mix and rice husk mix



R-1100P PROGRAMMABLE ELECTRICAL MUFFLE KILN USER MANUAL

Pic:1 FRONT VIEW:

Pic: 2 BACK VIEW:

TECHNICAL SPECIFICATIONS:

MODEL:	R-1100P	CALIBRATION:	YES
INPUT ON REQUEST:	115, 220 or 240 V	SOAKING PROCESS ACCURACY:	+/- 1 C
POWER:	3200 WATT	SAFETY MECHANISM:	Yes
ESTIMATED MAXIMUM HEATING TEMPERATURE:	1100 C / 2012 F	TEMPERATURE RANGE:	ROOM TEMPERATURE—1100 C / 2012 F
ESTIMATED HEATING TIME TO 1100 C:	90 MINUTES	VENTILATION SYSTEM:	DOOR HOLE
CONTROLLER TYPE:	PROGRAMMABLE, TWO-LINES	DIMENSIONS OF CHAMBER MM (INCH):	200(w) X 290(d) X 200(h) 8" x 11.3/5" x 8"
CONTINUOUSLY WORKING TIME ON 1100 C:	8 HOURS	DIMESIONS OF KILN MM (INCH):	360(w) X 450 (d) X 360(h) (14" x 18" x 14")
CONTINUOUSLY WORKIN TIME BELOW 1000 C:	12 HOURS	WEIGHT:	32 KG

Fig. A.1 Muffle kiln

Fig. A.2 is the assembly of the slow pyrolysis reactor covered by an electric heater. The electric heater was then attached to the control device as displayed in Figs. A.3 and A.4. The installation of the reactor and the control device can be seen in Fig. A.5.

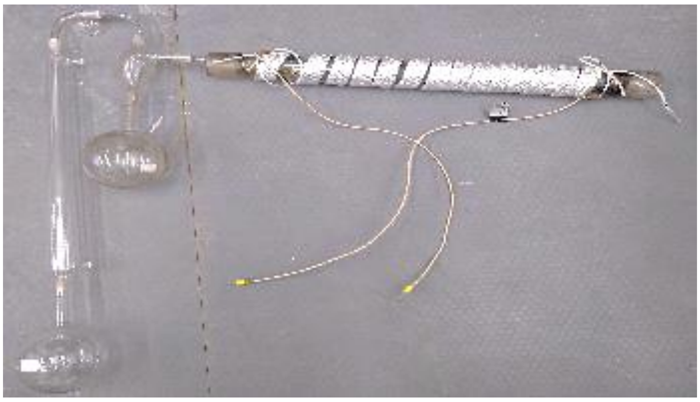


Fig. A.2 Reactor assembly

Fig. A.3 Control box cover

Fig.A.4 Control equipment

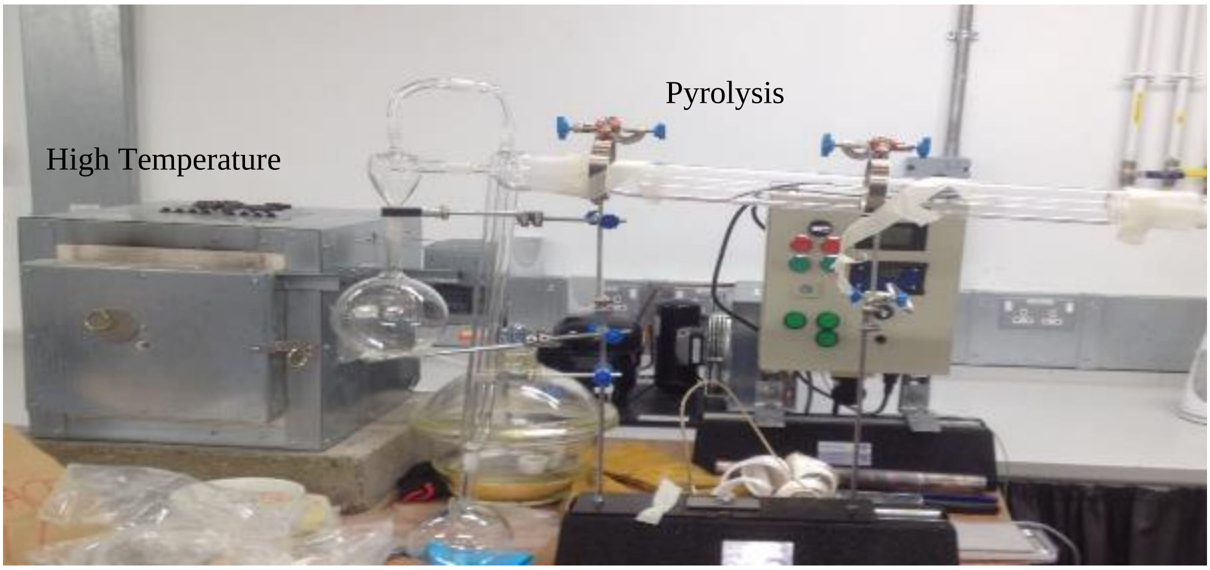


Fig. A.5 Experimental equipment in CSEF, Brunel University London

2. Pyrolysis equipment at the University of Limerick.

Figs. A.6 and A.7 show the pyrolysis reactor which was used for the PCL and FCL intermediate pyrolysis experiments at the University of Limerick. In Fig. A.7, the gas produced by the pyrolysis was not stored in a plastic bag but was passed through a paper-filled plastic bottle with the purpose to trap the aerosol in the gas yield. The liquid cooler seen in Fig. A.8 was used to condense the vapour of the pyrolysis process


Fig. A.6 Pyrolysis reactor with plastic bag collector


Fig. A.7 Pyrolysis reactor with aerosol collector

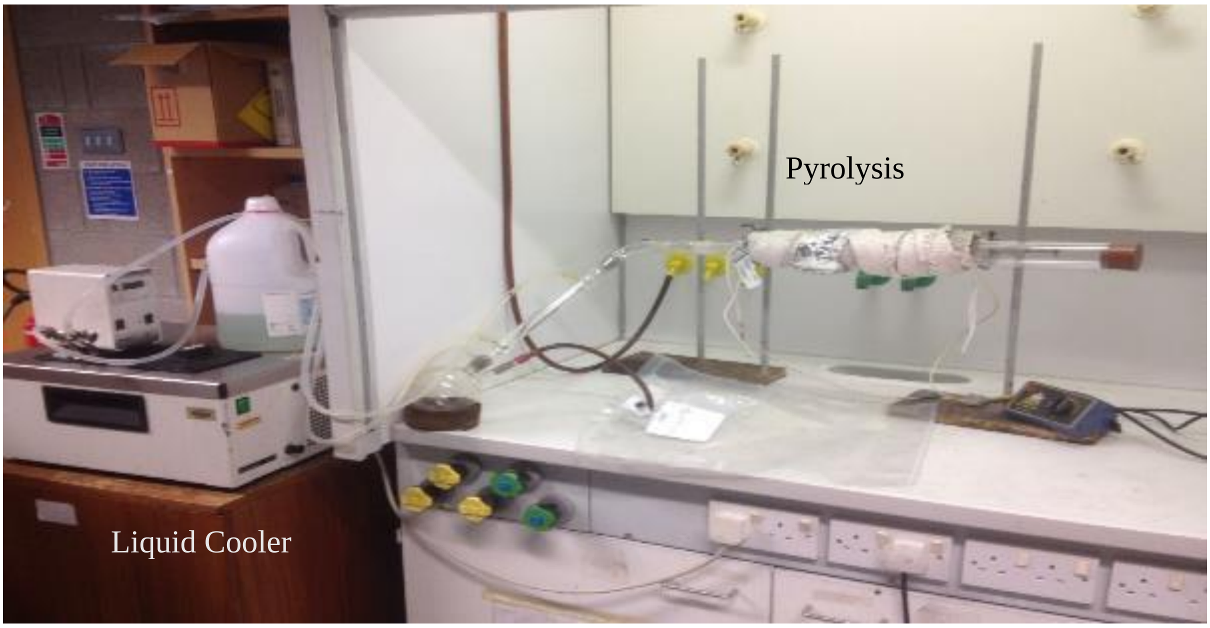


Fig. A.8 Experimental equipment at the University of Limerick

3. Pictures of experimental work at TU Delft.

Figs. A.9 to A.12 show activities conducted during the fast pyrolysis experiment at TU Delft, the Netherlands. Figure A.9 shows the grinding and sieving (< 100 µm) of the samples. The preparation of samples and the introduction to equipment was assisted by one of TU Delft’s

PhD students, Christos Tsekos. The next work is to prepare the fast pyrolysis by using Pyroprobe 5000 series (Figure A.10). Upon the completion of the experiment, the pre-analysis was performed for oil yield (Fig. A.11). Gas analysis was performed by using Varian CP-4900 Micro GC. (Fig A.12).

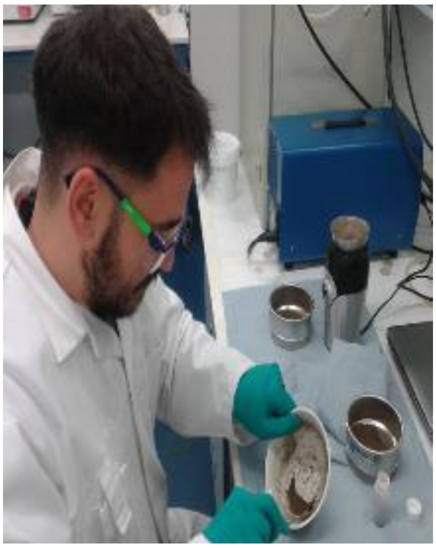


Fig. A.9 Sample preparation

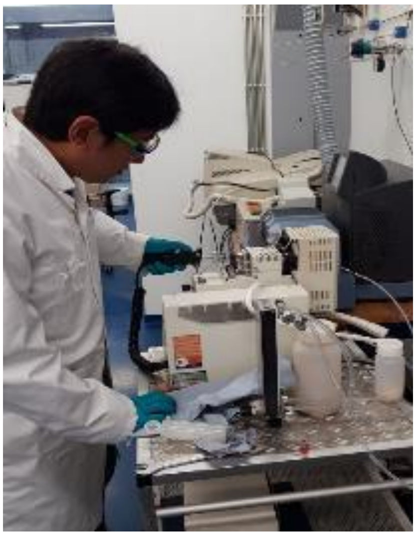


Fig. A.10 Pyroprobe preparation


Fig. A.11 Oil yield pre-analysis

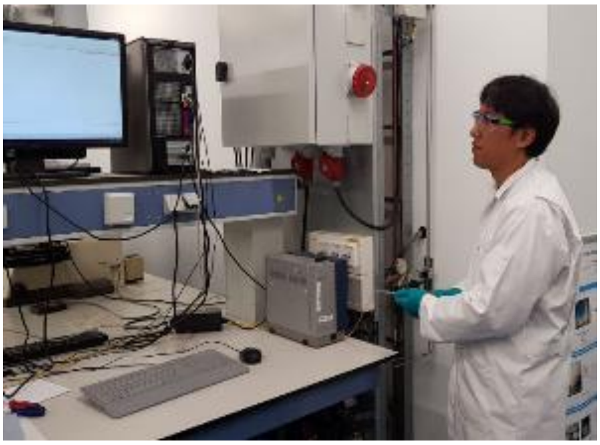


Fig. A.12 Gas yield analysis

4. Sample materials from pyrolysis.

Figs. A.13 to A.18 are some examples of the feedstock and yield products from the pyrolysis process.

Fig.A.13 Ground feedstock

Fig. A.14 Gas yield

Fig.A.15 liquid yield from slow pyrolysis

Fig. A.16 liquid yield from fast pyrolysis


Fig.A.17 Char yield from slow pyrolysis


Fig. A 18 Char yield from fast pyrolysis

Appendix B

All liquid yields resulting from slow and intermediate pyrolysis were tested it the laboratory of the Chemical Department, Bernal Institute, University of Limerick. The Chromatogram of the GC MSD, along with the identification table can be seen in this Appendix.

1. Oil yield Identification from slow pyrolysis (Sample from Brunel University London)

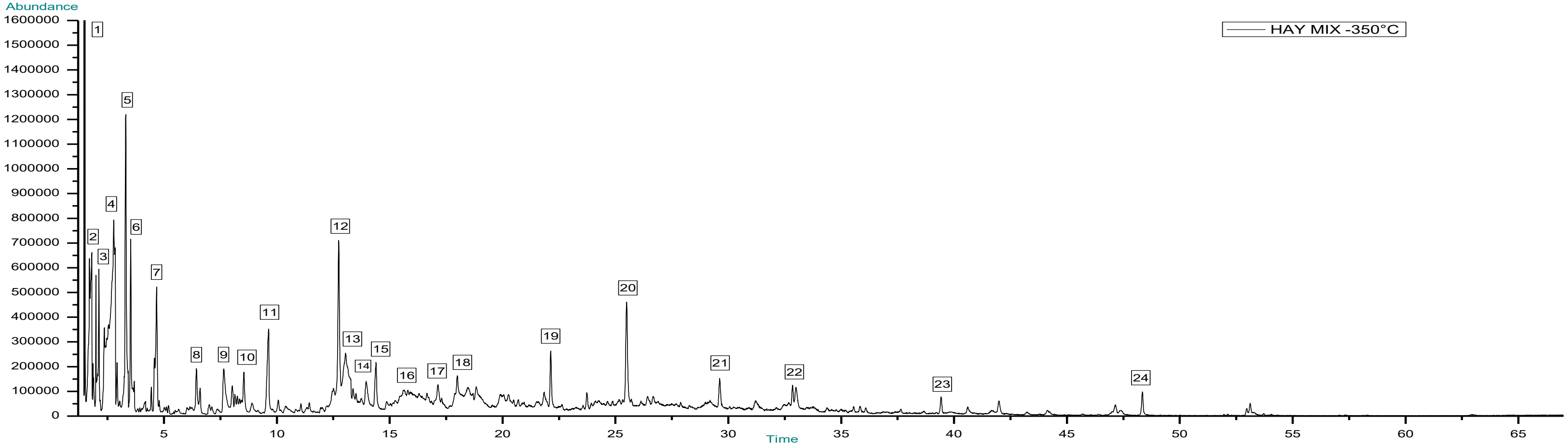


Table Compounds Identification of Oil from Hay Mix 350°C.

Compounds Name	Compounds Name	Compounds Name
1. Acetic acid ($C_2H_4O_2$)	9. Phenol (C_6H_6O)	17. Phenol, 3-ethyl- ($C_8H_{10}O$)
2. Propanoic acid ($C_3H_6O_2$)	10. 2-Furanmethanol, tetrahydro- ($C_5H_{10}O_2$)	18. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)
3. 1-Hydroxy-2-butanone ($C_4H_8O_2$)	11. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	19. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	12. Phenol, 2-methoxy- ($C_7H_8O_2$)	20. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
5. 2-Furanmethanol ($C_5H_6O_2$)	13. 1-Heptanol, 2-propyl- ($C_{10}H_{22}O$)	21. Phenol, 4-methoxy-3-(methoxymethyl)- ($C_9H_{12}O_3$)
6. 2-Propanone, 1-(acetyloxy)- ($C_5H_8O_3$)	14. Maltol ($C_6H_6O_3$)	22. Trimethoxyamphetamine, 2,3,5- ($C_{12}H_{19}NO_3$)
7. Butyrolactone ($C_4H_6O_2$)	15. 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	23. Phenol, 2,6-dimethoxy-4-(2-propenyl)- ($C_{11}H_{14}O_3$)
8. Furo[3,4-b]furan-2,6(3H,4H)-dione ($C_9H_{10}O_4$)	16. 4-Pyridinol (C_5H_5NO)	24. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)

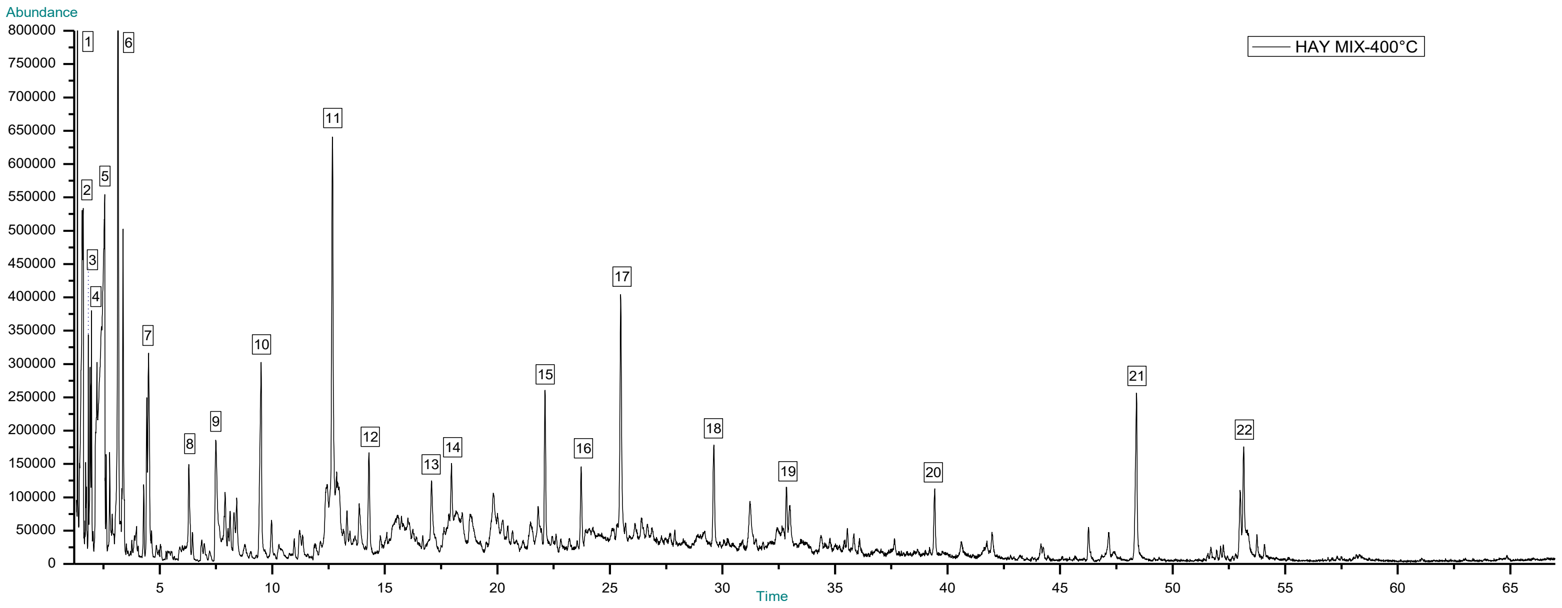


Table Compounds Identification of Oil from Hay Mix 400°C.

Compounds Name	Compounds Name	Compounds Name
1. Propanoic acid ($C_3H_6O_2$)	9. Phenol (C_6H_6O)	17. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
2. Pyridine (C_5H_5N)	10. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	18. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
3. 1-Hydroxy-2-butanone ($C_4H_8O_2$)	11. Phenol, 2-methoxy- ($C_7H_8O_2$)	19. Benzene, 1,2,3-trimethoxy-5-methyl- ($C_{10}H_{14}O_3$)
4. Hexanohydroxamic acid ($C_6H_{13}NO_2$)	12. 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	20. Phenol, 2,6-dimethoxy-4-(2-propenyl)- ($C_{11}H_{14}O_3$)
5. Butanoic acid ($C_4H_8O_2$)	13. Phenol, 3-ethyl- ($C_8H_{10}O$)	21. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
6. 2-Furanmethanol ($C_5H_6O_2$)	14. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	22. 9,12-Octadecadienoic acid (Z,Z)- ($C_{18}H_{32}O_2$)
7. Butyrolactone ($C_4H_6O_2$)	15. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	
8. 2-Cyclopenten-1-one, 3-methyl- (C_6H_8O)	16. 2-Methoxy-4-vinylphenol ($C_9H_{10}O_2$)	

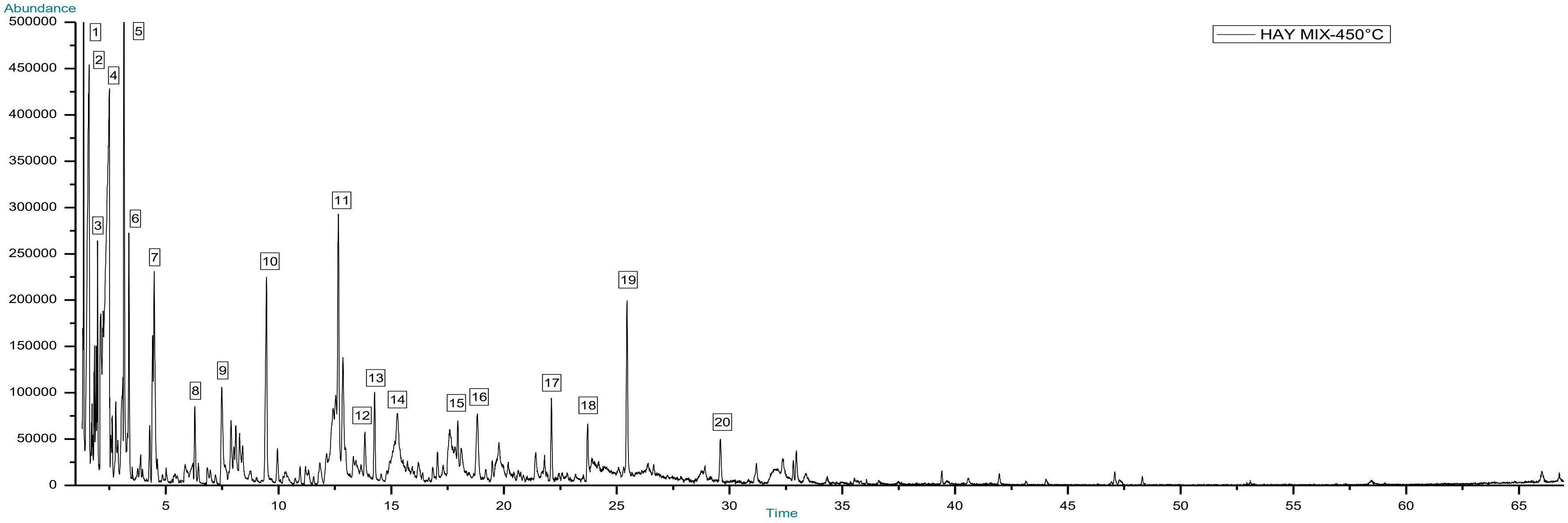


Table Compounds Identification of Oil from Hay Mix 450°C.

Compounds Name	Compounds Name	Compounds Name
1. Acetic acid, methyl ester ($C_3H_6O_2$)	8. 2-Cyclopenten-1-one, 3-methyl- (C_6H_8O)	15. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. Phenol (C_6H_6O)	16. 1,4:3,6-Dianhydro-α-d-glucopyranose ($C_6H_8O_4$)
3. Pyrazine ($C_4H_4N_2$)	10. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	17. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	11. Phenol, 2-methoxy- ($C_7H_8O_2$)	18. 2-Methoxy-4-vinylphenol ($C_9H_{10}O_2$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. Maltol ($C_6H_6O_3$)	19. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
6. 2-Propanone, 1-(acetyloxy)- ($C_5H_8O_3$)	13. 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	20. 1,2,3-Trimethoxybenzene ($C_9H_{12}O_3$)
7. Butyrolactone ($C_4H_6O_2$)	14. 4-Pyridinol (C_5H_5NO)	

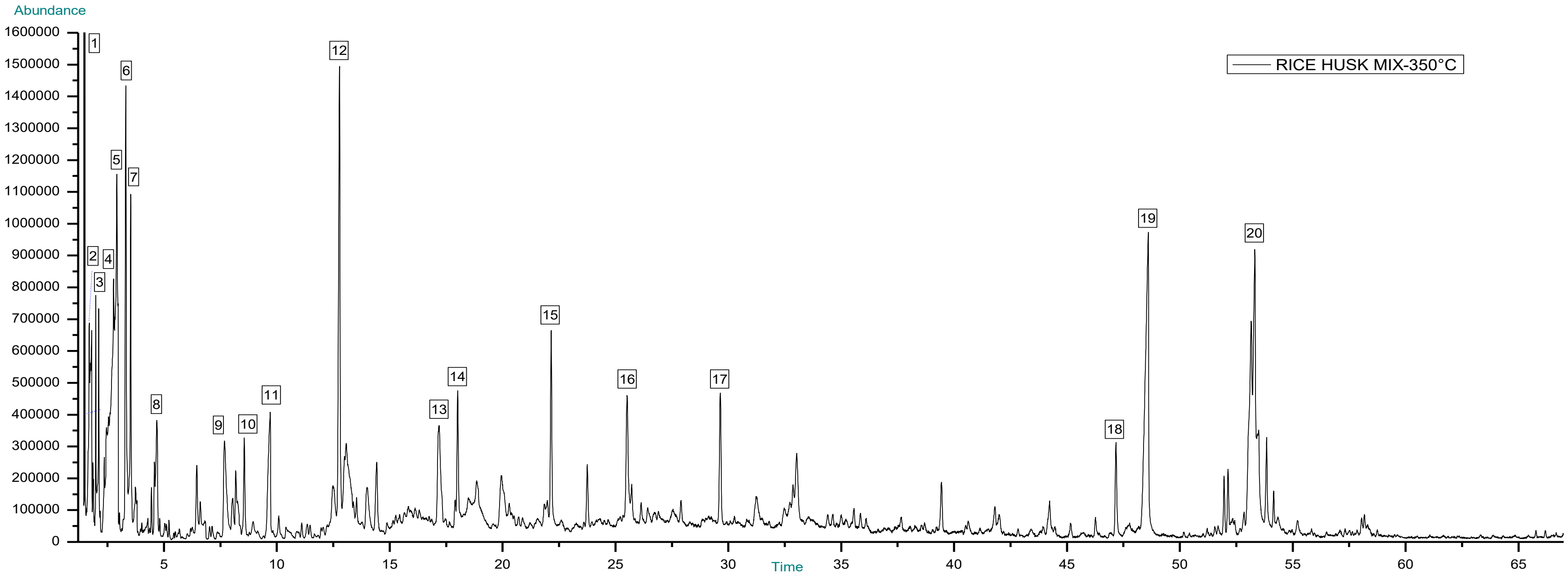


Table. Compounds Identification of Oil from Rice Husk Mix 350°C.

Compounds Name	Compounds Name	Compounds Name
1. Acetic acid ($C_2H_4O_2$)	8. Butyrolactone ($C_4H_6O_2$)	15. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. Phenol (C_6H_6O)	16. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
3. Pyridine (C_5H_5N)	10. 2-Furanmethanol, tetrahydro- ($C_5H_{10}O_2$)	17. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	11. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	18. Hexadecanoic acid, methyl ester ($C_{17}H_{34}O_2$)
5. 5-Hexenoic acid ($C_6H_{10}O_2$)	12. Phenol, 2-methoxy- ($C_7H_8O_2$)	19. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
6. 2-Furanmethanol ($C_5H_6O_2$)	13. Phenol, 4-ethyl- ($C_8H_{10}O$)	20. cis-Vaccenic acid ($C_{18}H_{34}O_2$)
7. 1,2-Ethanediol, diacetate ($C_6H_{10}O_4$)	14. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	

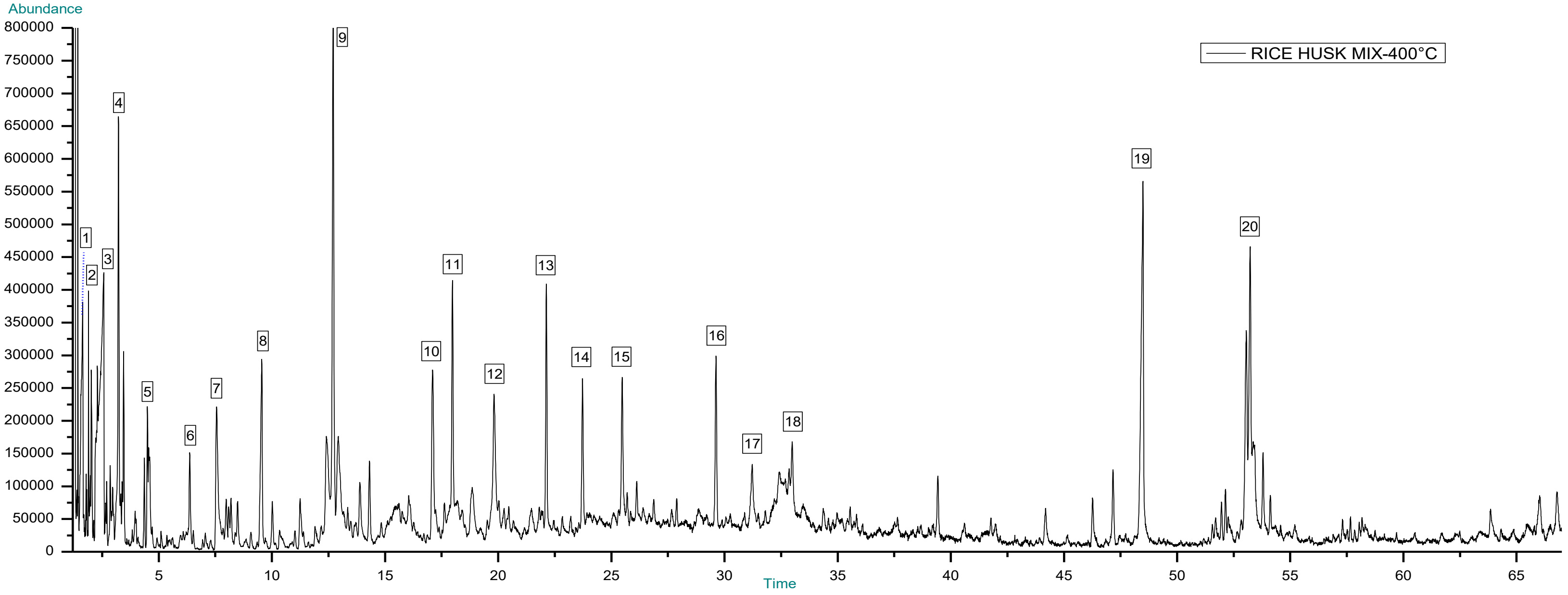


Table Compounds Identification of Oil from Rice Husk Mix 400°C.

Compounds Name	Compounds Name	Compounds Name
1. Propanoic acid ($C_3H_6O_2$)	8. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	15. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
2. Pyridine (C_5H_5N)	9. Phenol, 2-methoxy- ($C_7H_8O_2$)	16. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
3. Butanoic acid ($C_4H_8O_2$)	10. Phenol, 4-ethyl- ($C_8H_{10}O$)	17. Methyleugenol ($C_{11}H_{14}O_2$)
4. 2-Furanmethanol ($C_5H_6O_2$)	11. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	18. 4-Ethenyl-2,6-dimethoxyphenol ($C_{10}H_{12}O_3$)
5. 3-(5-Methylfuryl)-N-furamidopropionamide ($C_{13}H_{14}N_2O_4$)	12. Benzofuran, 2,3-dihydro- (C_8H_8O)	19. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
6. 2-Cyclopenten-1-one, 2-methyl- (C_6H_8O)	13. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	20. Oleic Acid ($C_{18}H_{34}O_2$)
7. Phenol (C_6H_6O)	14. 2-Methoxy-4-vinylphenol ($C_9H_{10}O_2$)	

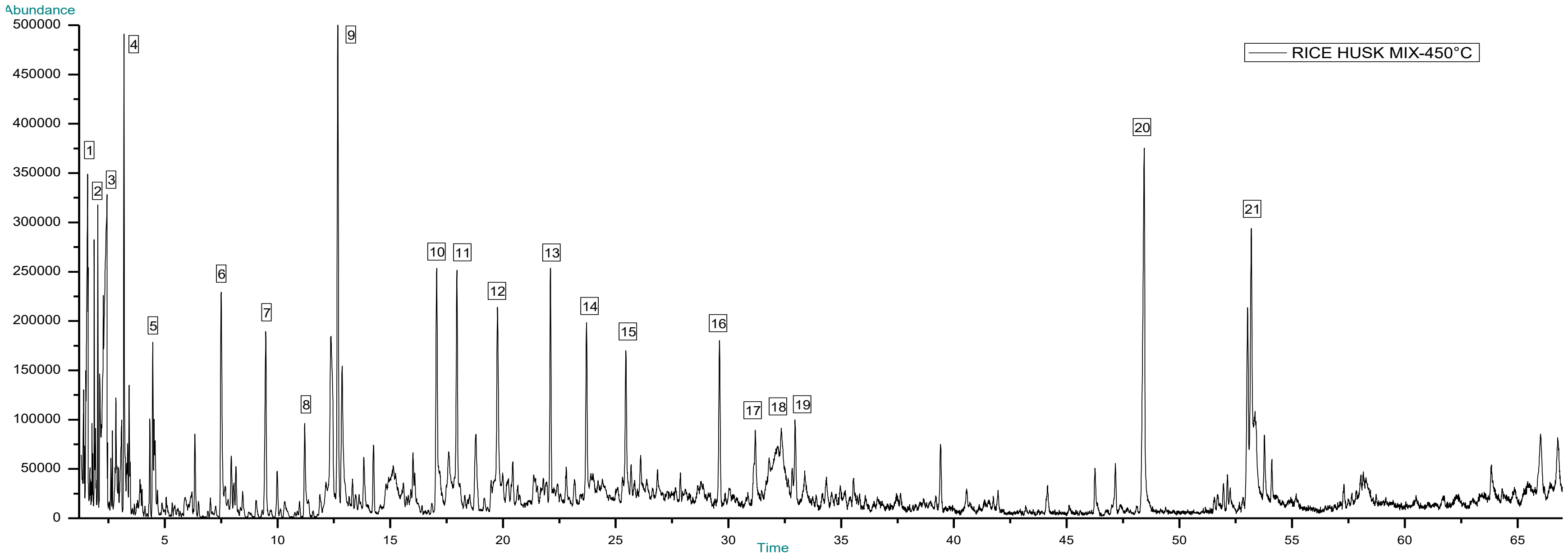


Table Compounds Identification of Oil from Rice Husk Mix 450°C.

Compounds Name	Compounds Name	Compounds Name
1. Propanoic acid ($C_3H_6O_2$)	8. Phenol, 2-methyl- (C_7H_8O)	15. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
2. Toluene (C_7H_8)	9. Phenol, 2-methoxy- ($C_7H_8O_2$)	16. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
3. Butanoic acid ($C_4H_8O_2$)	10. Phenol, 4-ethyl- ($C_8H_{10}O$)	17. 4-(2,3-Dimethyl-2-butanyl)phenol ($C_{12}H_{18}O$)
4. 2-Furanmethanol ($C_5H_6O_2$)	11. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	18. 2-Propenoic acid, 3- (4-hydroxyphenyl)- ($C_9H_8O_3$)
5. Pyrazine, 2,5-dimethyl ($C_6H_8N_2$)	12. Phenol, 4-ethyl- ($C_8H_{10}O$)	19. 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)
6. Phenol (C_6H_6O)	13. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	20. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
7. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	14. Benzofuran, 2,3-dihydro- (C_8H_8O)	21. Oleic Acid ($C_{18}H_{34}O_2$)

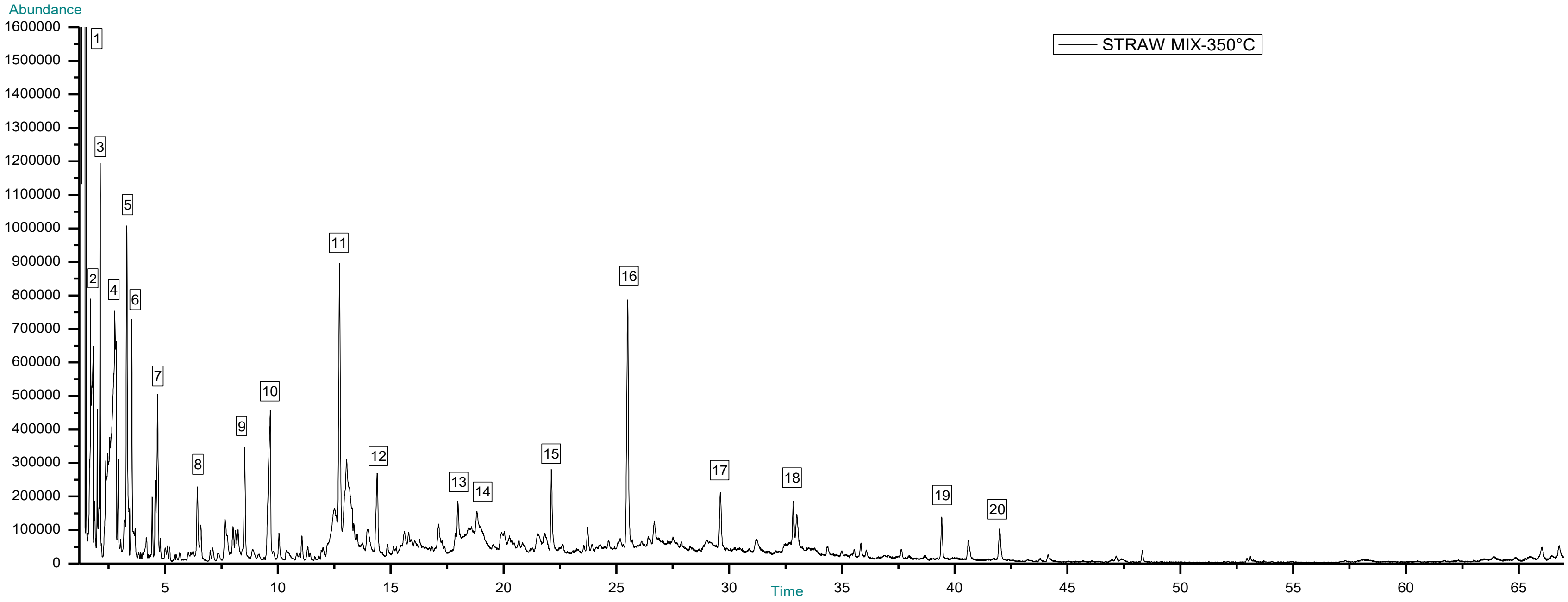


Table Compounds Identification of Oil from Straw Mix 350°C.

Compounds Name	Compounds Name	Compounds Name
1. Acetic acid ($C_2H_4O_2$)	8. 2-Cyclopenten-1-one, 2-methyl- (C_6H_8O)	15. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. Furan-2-carbonyl chloride, tetrahydro- ($C_5H_7ClO_2$)	16. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
3. 1-Hydroxy-2-butanone ($C_4H_8O_2$)	10. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	17. Phenol, 4-methoxy-3-(methoxymethyl)- ($C_9H_{12}O_3$)
4. Butanoic acid ($C_4H_8O_2$)	11. Phenol, 2-methoxy- ($C_7H_8O_2$)	18. Benzene, 1,2,3-trimethoxy-5-methyl- ($C_{10}H_{14}O_3$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	19. Phenol, 2,6-dimethoxy-4-(2-propenyl)- ($C_{11}H_{14}O_3$)
6. 2-Propanone, 1-(acetyloxy)- ($C_5H_8O_3$)	13. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	20. 2-Pentanone, 1-(2,4,6-trihydroxyphenyl) ($C_{11}H_{14}O_4$)
7. Butyrolactone ($C_4H_6O_2$)	14. 7-Octene-2,4-dione ($C_8H_{12}O_2$)	

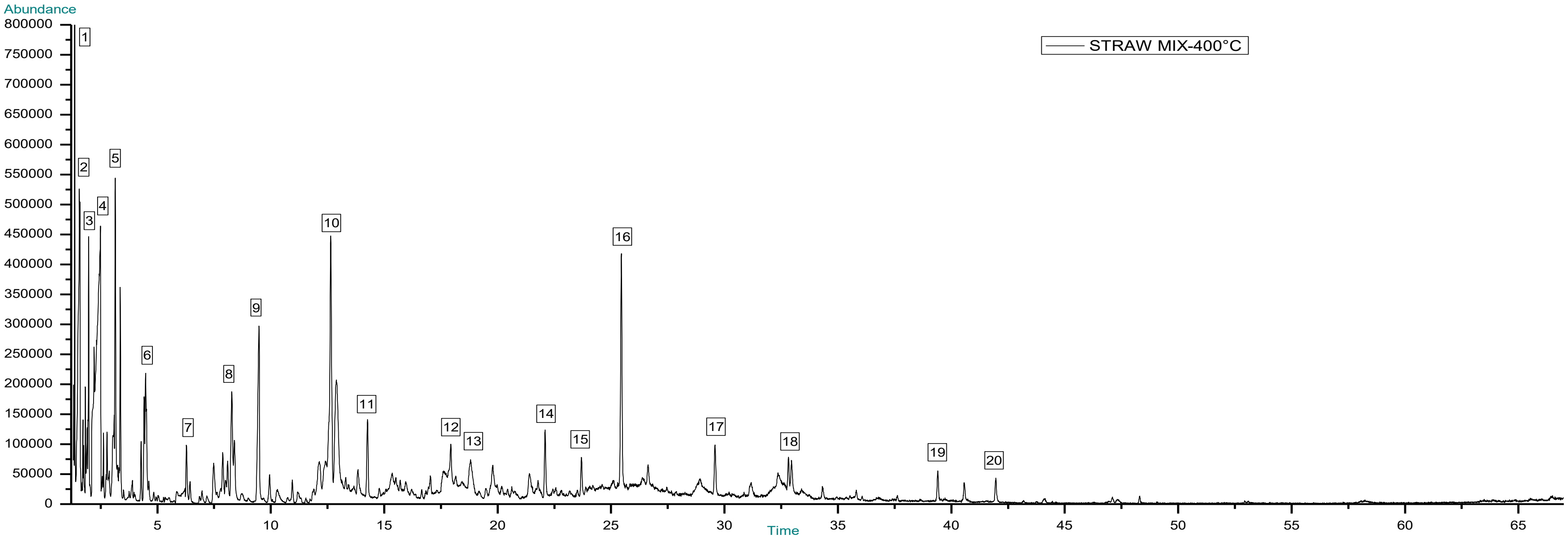


Table Compounds Identification of Oil from Straw Mix 400°C.

Compounds Name	Compounds Name	Compounds Name
1. Acetic acid ($C_2H_4O_2$)	8. 2,4-Dimethyl-2-oxazoline-4-methanol ($C_6H_{11}NO_2$)	15. 2-Methoxy-4-vinylphenol ($C_9H_{10}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	16. : Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
3. 1-Hydroxy-2-butanone ($C_4H_8O_2$)	10. Phenol, 2-methoxy- ($C_7H_8O_2$)	17. Phenol, 4-methoxy-3-(methoxymethyl)- ($C_9H_{12}O_3$)
4. Butanoic acid (Butanoic acid)	11. 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	18. Benzene, 1,2,3-trimethoxy-5-methyl- ($C_{10}H_{14}O_3$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	19. Phenol, 2,6-dimethoxy-4-(2-propenyl)- ($C_{11}H_{14}O_3$)
6. Butyrolactone ($C_4H_6O_2$)	13. 1,4:3,6-Dianhydro-α-d-glucopyranose ($C_6H_8O_4$)	20. Desaspidinol ($C_{11}H_{14}O_4$)
7. 2-Cyclopenten-1-one, 3-methyl- (C_6H_8O)	14. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	

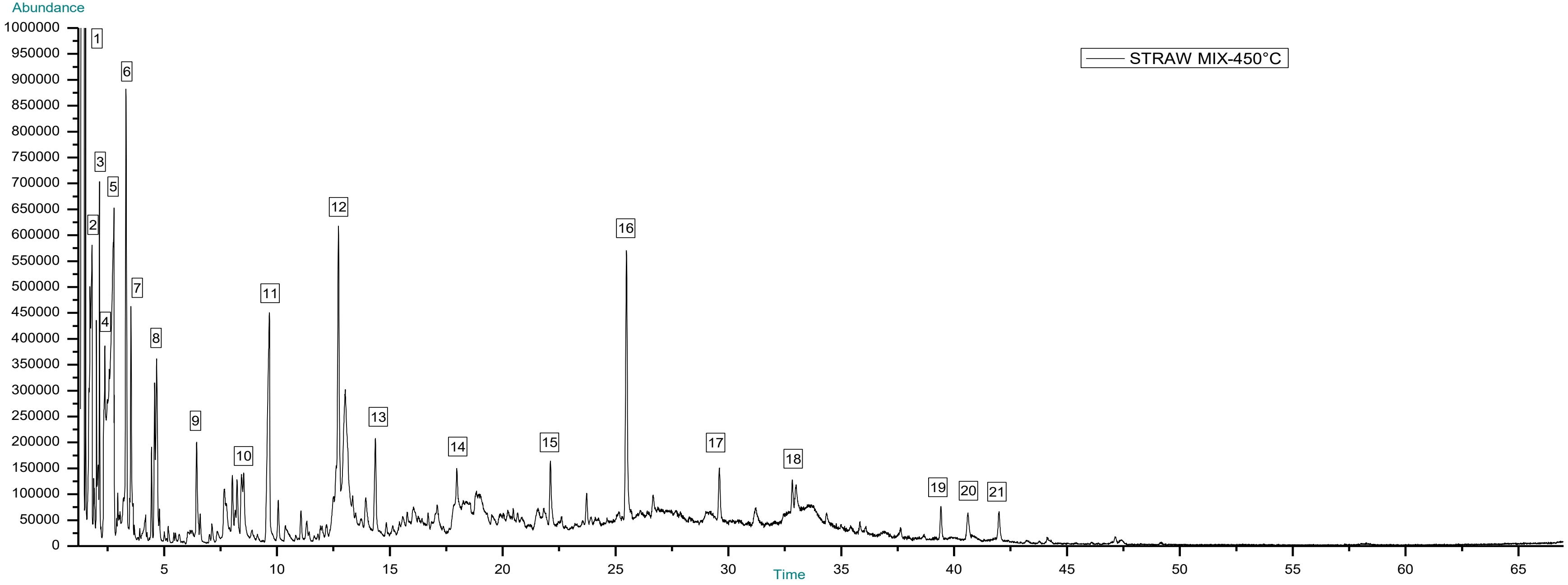


Table Compounds Identification of Oil from Straw Mix 450°C.

Compounds Name	Compounds Name	Compounds Name
1. Hexadecanamide ($C_{16}H_{33}NO$)	8. Butyrolactone ($C_4H_6O_2$)	15. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. 2-Cyclopenten-1-one, 3-methyl- (C_6H_8O)	16. Phenol, 2,6-dimethoxy- ($C_8H_{10}O_3$)
3. Propanoic acid ($C_3H_6O_2$)	10. 2-(3-Methylbutyl)-3,5-dimethylpyrazine ($C_{11}H_{18}N_2$)	17. Phenol, 4-methoxy-3-(methoxymethyl)- ($C_9H_{12}O_3$)
4. Propanoic acid ($C_3H_6O_2$)	11. 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- ($C_6H_8O_2$)	18. Benzene, 1,2,3-trimethoxy-5-methyl- ($C_{10}H_{14}O_3$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. Phenol, 2-methoxy- ($C_7H_8O_2$)	19. Phenol, 2,6-dimethoxy-4-(2-propenyl)- ($C_{11}H_{14}O_3$)
6. 1,2-Ethanediol, diacetate ($C_6H_{10}O_4$)	13. 2-Cyclopenten-1-one, 3-ethyl-2-hydroxy- ($C_7H_{10}O_2$)	20. Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- ($C_{10}H_{12}O_4$)
7. 2-Propanone, 1-(acetyloxy)- ($C_5H_8O_3$)	14. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	21. 2-Pentanone, 1-(2,4,6-trihydroxyphenyl) ($C_{11}H_{14}O_4$)

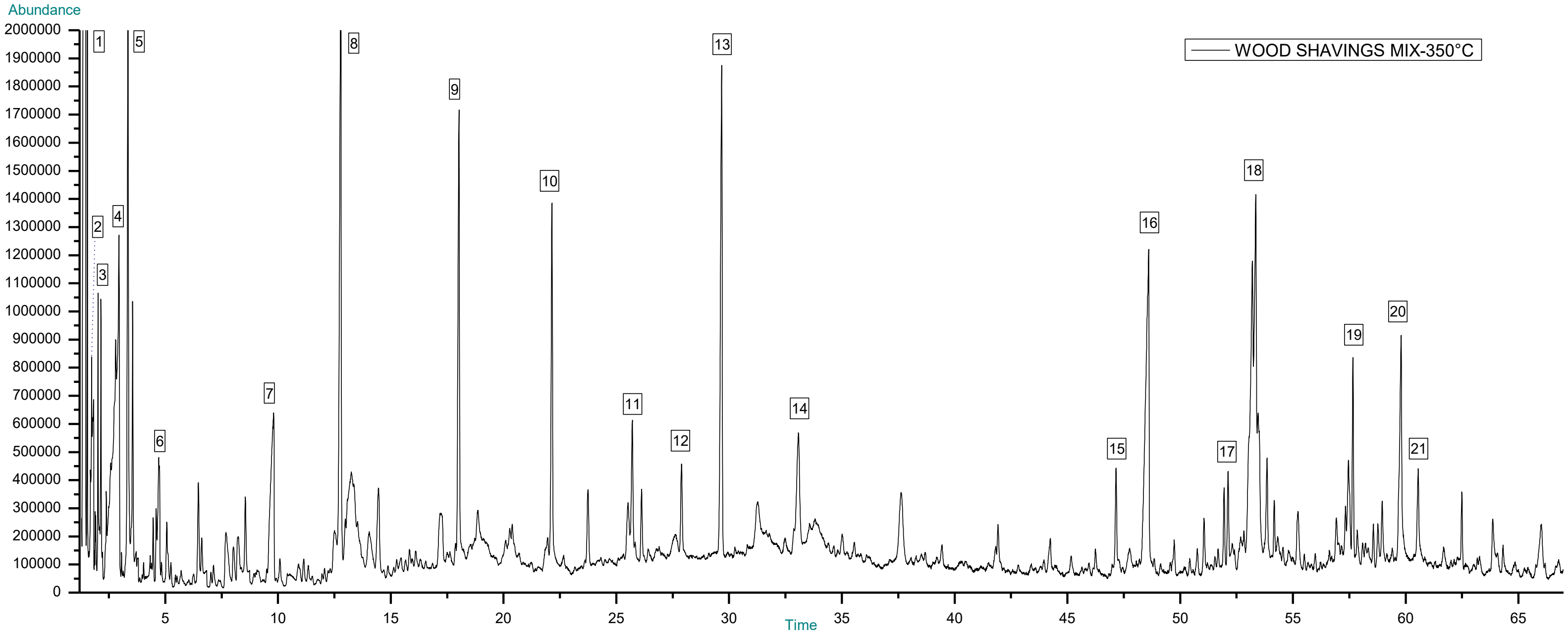


Table Compounds Identification of Oil from Wood Savings Mix 350°C.

Compounds Name	Compounds Name	Compounds Name
1. 2-Propanone, 1-hydroxy- ($C_3H_6O_2$)	8. Phenol, 2-methoxy- ($C_7H_8O_2$)	15. Pentadecanoic acid, 14-methyl-, methyl ester ($C_{17}H_{34}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	16. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
3. Pyridine (C_5H_5N)	10. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	17. 10-Octadecenoic acid, methyl ester ($C_{19}H_{36}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	11. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	18. Oleic Acid ($C_{18}H_{34}O_2$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	19. Dronabinol ($C_{21}H_{30}O_2$)
6. Cyclopentanone (C_5H_8O)	13. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	20. Retinoic acid ($C_{20}H_{28}O_2$)
7. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	14. 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)	21. Abietic acid ($C_{20}H_{30}O_2$)

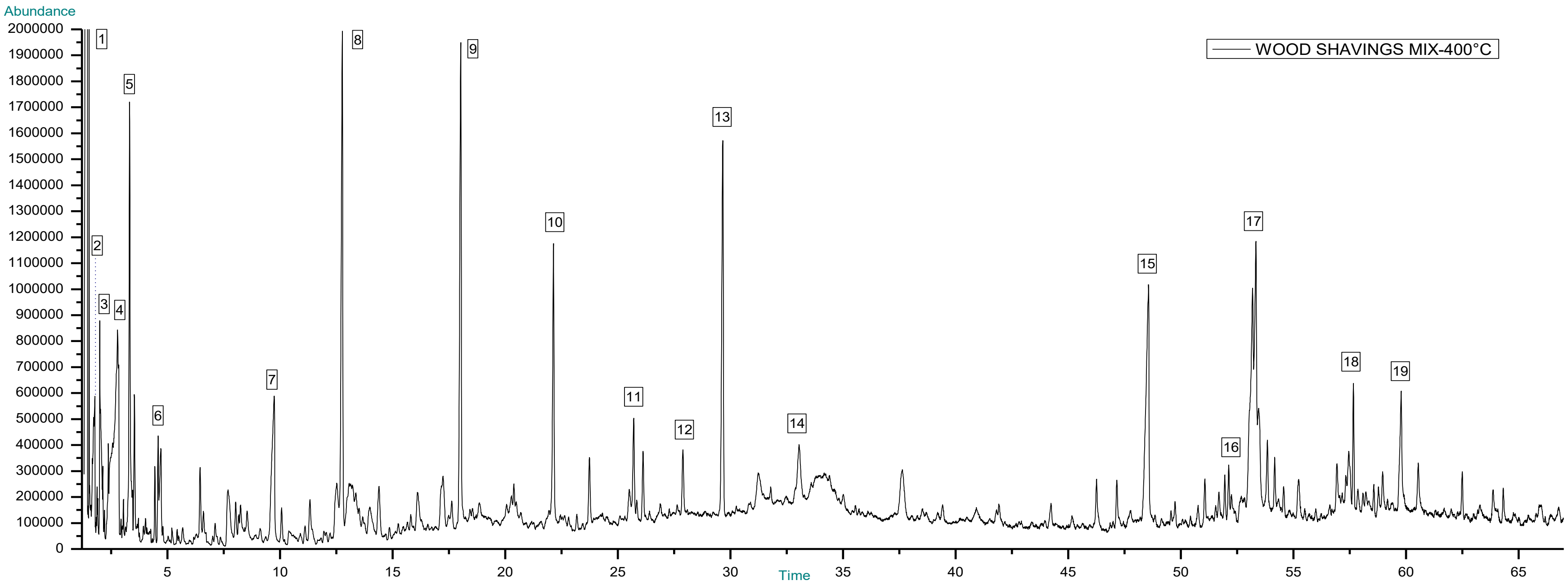


Table Compounds Identification of Oil from Wood Savings Mix 400°C.

Compounds Name	Compounds Name	Compounds Name
1. Furan, 2,5-dimethyl- (C_6H_8O)	8. Cyclopentanol ($C_5H_{10}O$)	15. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	16. 10-Octadecenoic acid, methyl ester ($C_{19}H_{36}O_2$)
3. Pyridine (C_5H_5N)	10. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	17. Oleic Acid ($C_{18}H_{34}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	11. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	18. Dronabinol ($C_{21}H_{30}O_2$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	19. Retinoic acid ($C_{20}H_{28}O_2$)
6. Pyrazine, 2,6-dimethyl- ($C_6H_8N_2$)	13. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	
7. 1,2-Cyclopentanedione, 3-methyl- ($C_6H_8O_2$)	14. 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- ($C_{10}H_{12}O_3$)	

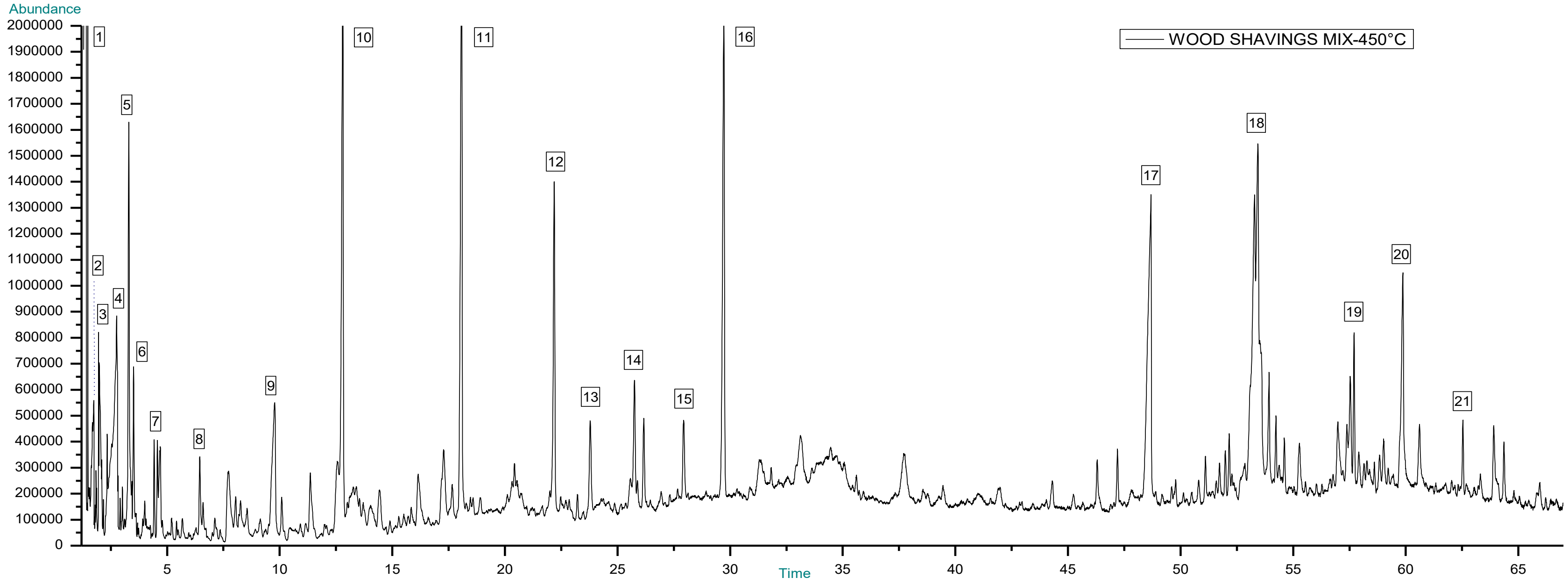


Table Compounds Identification of Oil from Wood Savings Mix 450°C.

Compounds Name	Compounds Name	Compounds Name
1. Acetic acid ($C_2H_4O_2$)	8. 2-Cyclopenten-1-one, 2-methyl- (C_6H_8O)	15. Phenol, 2-methoxy-5-(1-propenyl)-, (E)- ($C_{10}H_{12}O_2$)
2. Propanoic acid ($C_3H_6O_2$)	9. 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- ($C_6H_8O_2$)	16. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)
3. Pyridine (C_5H_5N)	10. Phenol, 2-methoxy- ($C_7H_8O_2$)	17. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
4. Butanoic acid ($C_4H_8O_2$)	11. Phenol, 2-methoxy-4-methyl- ($C_8H_{10}O_2$)	18. Oleic Acid ($C_{18}H_{34}O_2$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. Phenol, 4-ethyl-2-methoxy- ($C_9H_{12}O_2$)	19. Dronabinol ($C_{21}H_{30}O_2$)
6. 2-Propanone, 1-(acetyloxy)- ($C_5H_8O_3$)	13. 2-Methoxy-4-vinylphenol ($C_9H_{10}O_2$)	20. Retinoic acid ($C_{20}H_{28}O_2$)
7. 2-Cyclopenten-1-one, 2-methyl- (C_6H_8O)	14. Phenol, 2-methoxy-4-(1-propenyl)- ($C_{10}H_{12}O_2$)	21. Pyrethrin 1 ($C_{21}H_{28}O_3$)

2. Oil yield Identification from intermediate pyrolysis (Sample from University of Limerick)

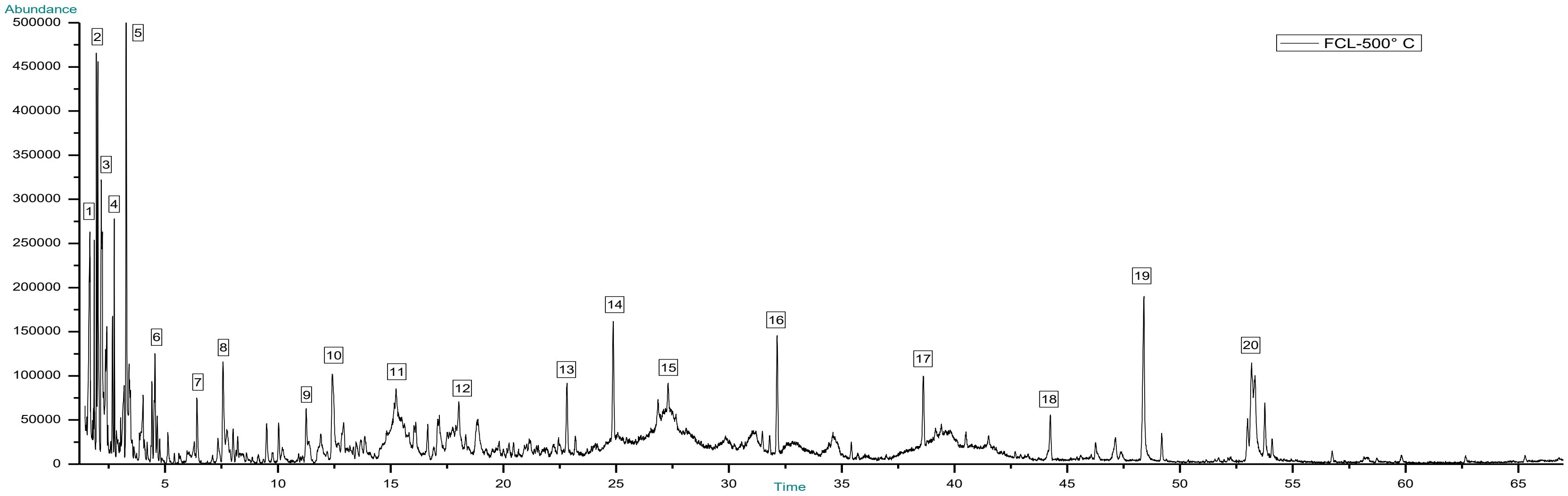


Table Compounds Identification of Oil from FCL 500°C.

Compounds Name	Compounds Name	Compounds Name
1. 2-Propanoic acid ($C_3H_4O_2$)		14. Cyclohexasiloxane, dodecamethyl- ($C_{12}H_{36}O_6Si_6$)
	7. 2-Cyclopenten-1-one, 3-methyl- (C_6H_8O)	15. Piperazine-2,5-dione ($C_4H_6N_2O_2$)
2. Pyridine (C_5H_5N)	8. Phenol (C_6H_6O)	16. Cycloheptasiloxane, tetradecamethyl- ($C_{14}H_{42}O_7Si_7$)
	9. Phenol, 2-methyl- (C_7H_8O)	17. Cyclooctasiloxane, hexadecamethyl- ($C_{16}H_{48}O_8Si_8$)
3. Acetamide (C_2H_5NO)	10. Phenol, 3-methyl- (C_7H_8O)	18. Cyclononasiloxane, octadecamethyl- ($C_{18}H_{54}O_9Si_9$)
4. Pyrazine, methyl ($C_5H_6N_2$)	11. 3-Pyridinol (C_5H_5NO)	19. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
5. 2-Furanmethanol ($C_5H_6O_2$)	12. 2/3-Trifluoroacetoxydodecane ($C_4H_{25}F_3O_2$)	20. 9,12-Octadecadienoic acid (Z,Z)- (C18H32O2)
	13. Indolizine (C_8H_7N)	

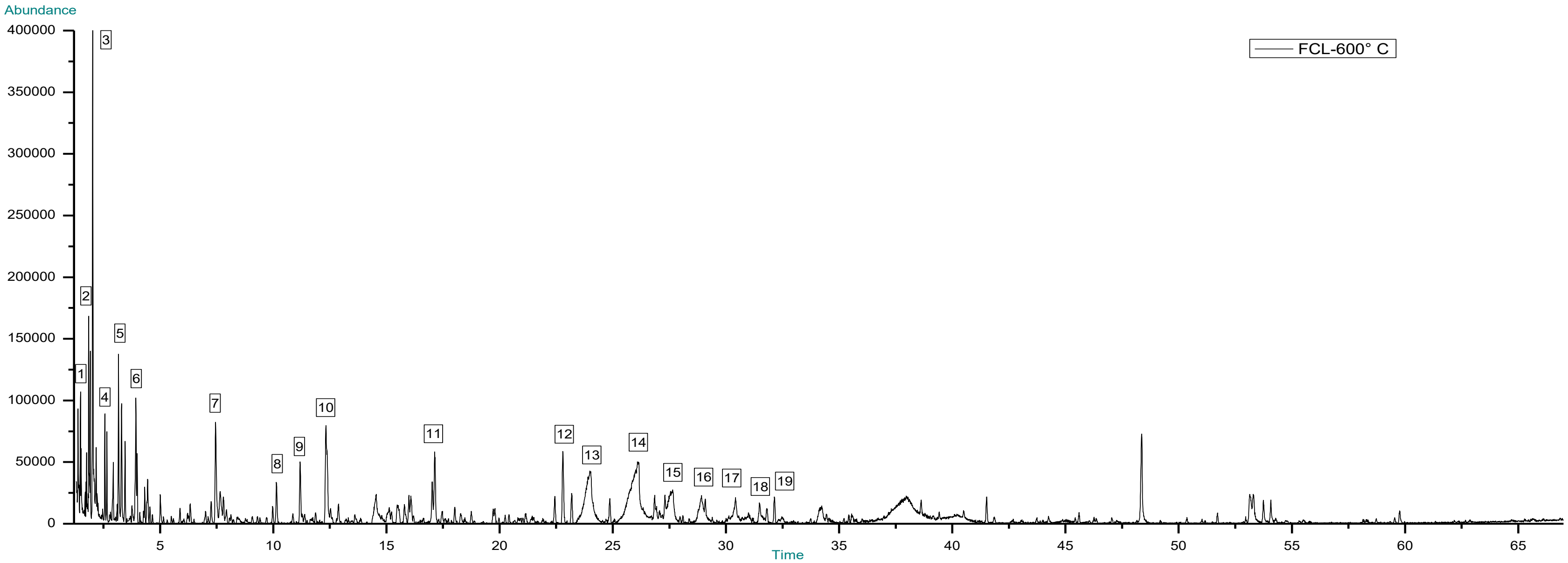


Table Compounds Identification of Oil from FCL 600°C.

Compounds Name	Compounds Name	Compounds Name
1. Propanoic acid ($C_3H_6O_2$)	8. Benzene, 1-ethynyl-4-methyl (C_9H_8)	15. 2,4-Imidazolidinedione, 5-ethyl-5-methyl- ($C_6H_{10}N_2O_2$)
	9. Phenol, 2-methyl- (C_7H_8O)	16. N,N’-trimethylene-urea ($C_4H_8N_2O$)
2. Pyridine (C_5H_5N)	10. Phenol, 4-methyl- (C_7H_8O)	17. 6-Undecylamine ($C_{11}H_{25}N$)
	11. Naphthalene ($C_{10}H_8$)	18. Octane (C_8H_{18})
3. Toluene (C_7H_8)	12. Indole (C_8H_7N)	19. Cycloheptasiloxane, tetradecamethyl- ($C_{14}H_{42}O_7Si_7$)
4. Pyridine 2-Methyl- (C_6H_7N)	13. 2,4 -Imidazolidinedione,5,5-dimethyl- ($C_5H_8N_2O_2$)	
5. 2-Furanmethanol ($C_5H_6O_2$)	14. 2,4 -Imidazolidinedione, 5-methyl- ($C_6H_6N_2O_2$)	
6. Styrene (C_8H_8)		

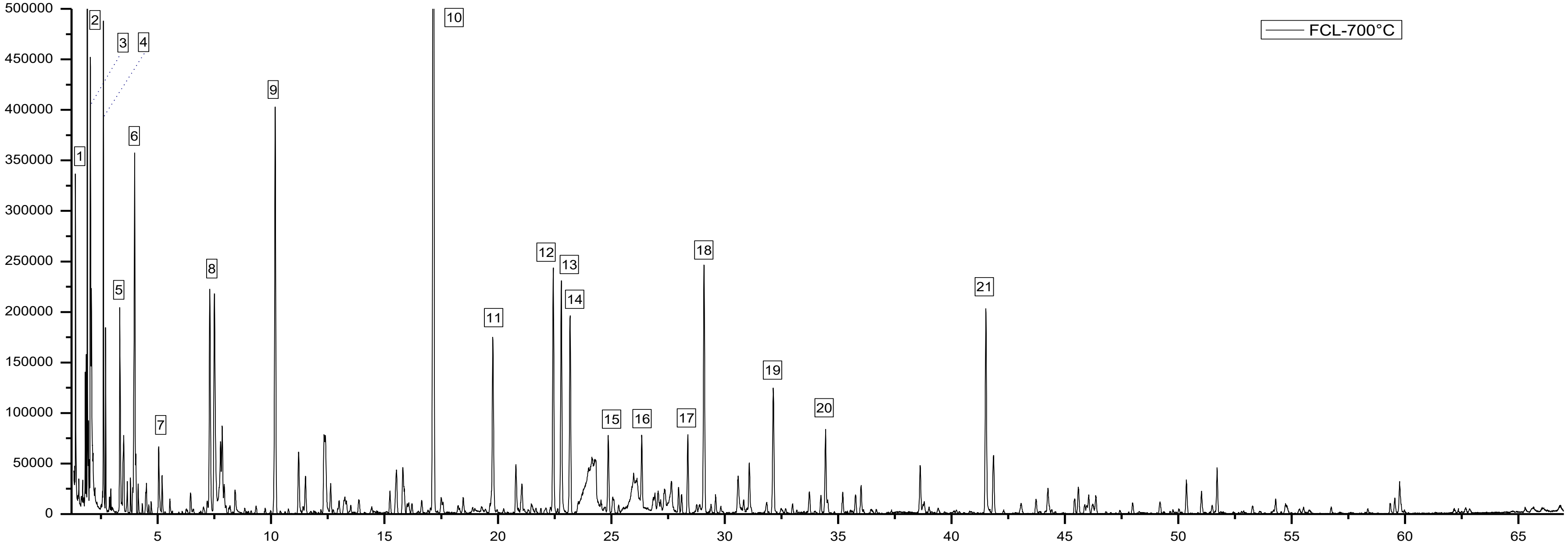


Table Compounds Identification of Oil from FCL 700°C.

Compounds Name	Compounds Name	Compounds Name
1. Benzene (C_6H_6)	8. Benzonitrile (C_7H_5N)	15. 2,4-Imidazolidinedione, 5,5-dimethyl- ($C_5H_8N_2O_2$)
2. Pyridine (C_5H_5N)	9. Benzene, 1-propynyl- (C_9H_8)	16. Biphenyl ($C_{12}H_{10}$)
3. Toluene (C_7H_8)	10. Naphthalene ($C_{10}H_8$)	17. Biphenyl ($C_{12}H_{10}$)
4. Pyridine, 2-methyl- (C_6H_7N)	11. Quinoline (C_9H_7N)	18. Biphenylene ($C_{12}H_8$)
5. Pyridine (C_5H_5N)	12. Naphthalene, 2-methyl- ($C_{11}H_{10}$)	19. Cycloheptasiloxane, tetradecamethyl- ($C_{14}H_{42}O_7Si_7$)
6. Styrene (C_8H_8)	13. Indole (C_8H_7N)	20. Fluorene ($C_{13}H_{10}$)
7. Pyridine, 2,4-dimethyl- (C_7H_9N)	14. Naphthalene, 2-methyl- ($C_{11}H_{10}$)	21. Anthracene ($C_{14}H_{10}$)

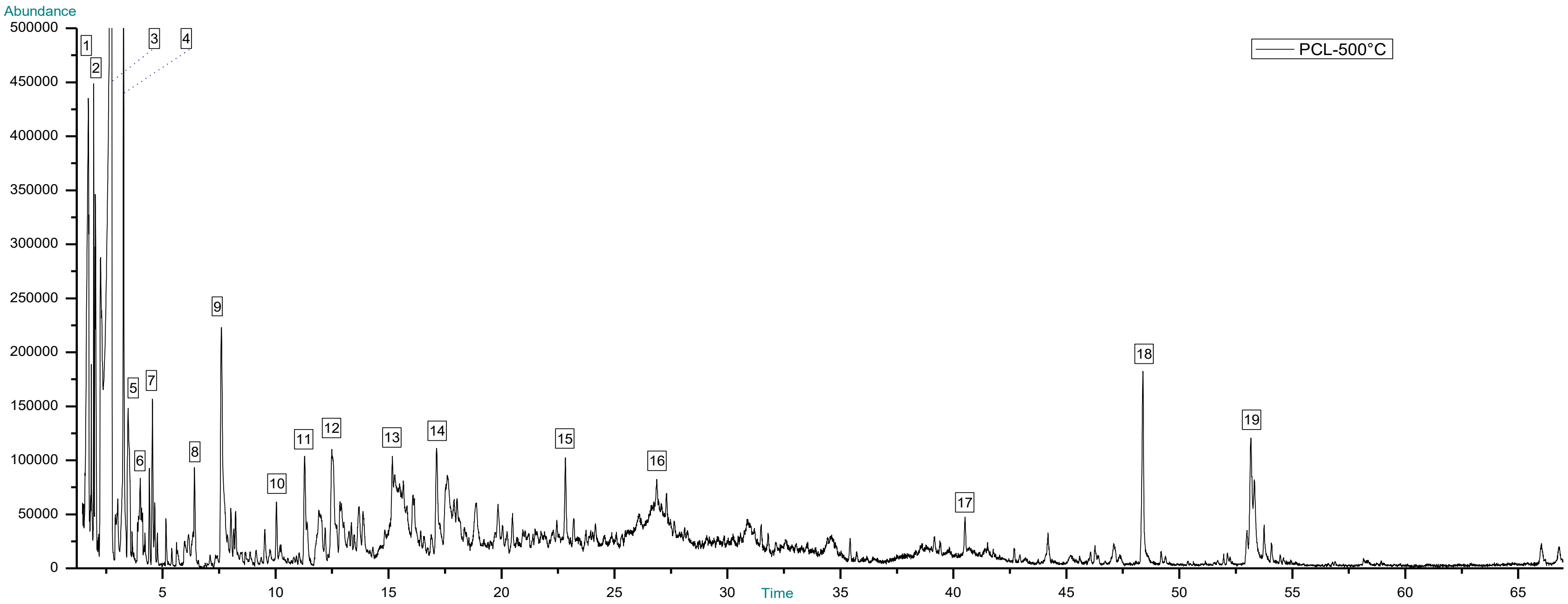


Table Compounds Identification of Oil from PCL 500°C.

Compounds Name	Compounds Name	Compounds Name
1. Propanoic acid ($C_3H_6O_2$)	8. 2-Cyclopenten-1-one, 3-methyl- (C_6H_8O)	15. Indolizine (C_8H_7N)
2. Pyridine (C_5H_5N)	9. Phenol (C_6H_6O)	16. 1-Piperidinoacetylindoline ($C_{15}H_{20}N_2O$)
3. Butanoic acid ($C_4H_8O_2$)	10. 2-Cyclopenten-1-one, 2,3-dimethyl- ($C_7H_{10}O$)	17. Trichloroacetic acid, tridecyl ester ($C_{15}H_{27}Cl_3O_2$)
4. 2-Furanmethanol ($C_5H_6O_2$)	11. Phenol, 2-methyl- (C_7H_8O)	18. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
5. 4-Methylene-5-methylthiomethylcyclohexene ($C_9H_{14}S$)	12. Phenol, 3-methyl- (C_7H_8O)	19. Oleic Acid ($C_{18}H_{34}O_2$)
6. Styrene (C_8H_8)	13. 3-Hydroxypyridine-N-oxide ($C_5H_5NO_2$)	
7. Pyrazine, 2,5-dimethyl- ($C_6H_8N_2$)	14. Phenol, 3-ethyl- ($C_8H_{10}O$)	

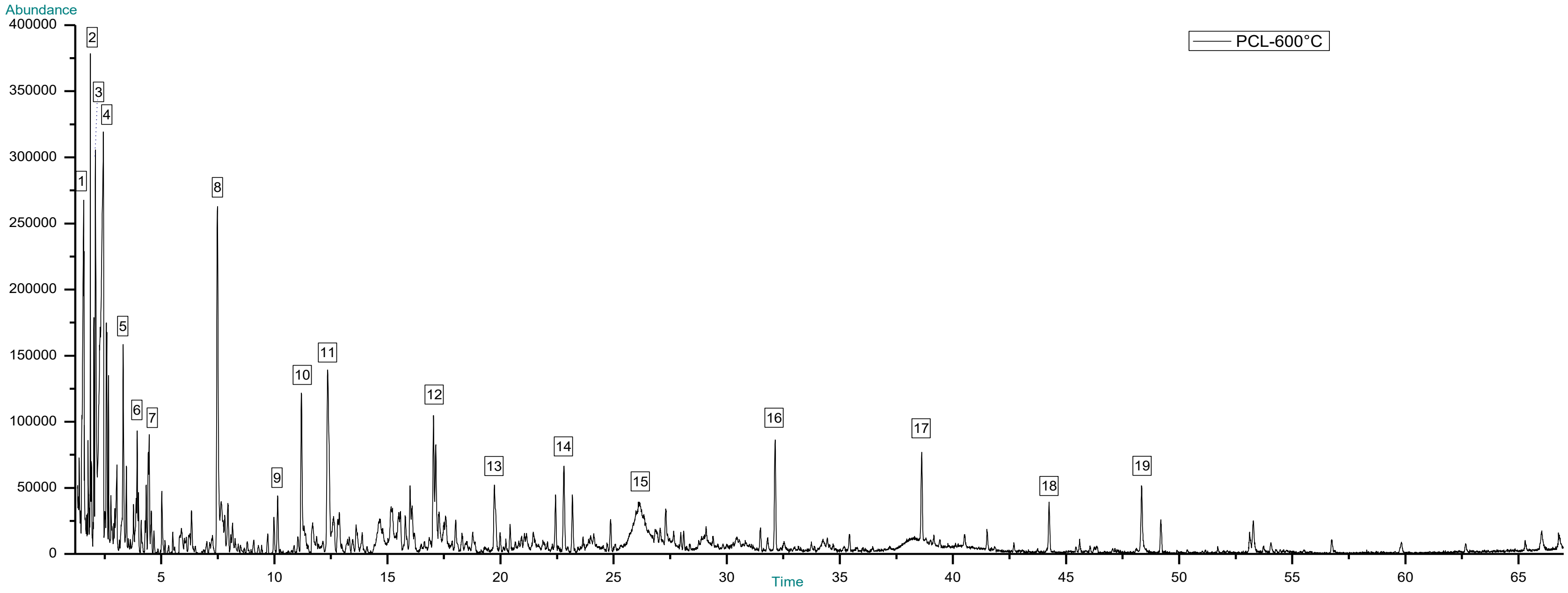


Table Compounds Identification of Oil from PCL 600°C.

Compounds Name	Compounds Name	Compounds Name
1. Propanoic acid ($C_3H_6O_2$)	8. Phenol (C_6H_6O)	15. 2,4-Imidazolidinedione, 5-methyl- ($C_4H_6N_2O_2$)
2. Acetamide (C_2H_5NO)	9. Indene (C_9H_8)	16. Cycloheptasiloxane, tetradecamethyl- ($C_{14}H_{42}O_7Si_7$)
3. Butanoic acid ($C_4H_8O_2$)	10. Phenol, 2-methyl- (C_7H_8O)	17. Cyclooctasiloxane, hexadecamethyl- ($C_{16}H_{48}O_8Si_8$)
4. Pyrimidine, 2-methyl- ($C_5H_6N_2$)	11. Phenol, 4-methyl- (C_7H_8O)	18. Cyclononasiloxane, octadecamethyl- ($C_{18}H_{54}O_9Si_9$)
5. Pyridine, 3-methyl- (C_6H_7N)	12. Phenol, 4-ethyl- ($C_8H_{10}O$)	19. n-Hexadecanoic acid ($C_{16}H_{32}O_2$)
6. Styrene (C_8H_8)	13. Benzofuran, 2,3-dihydro- (C_8H_8O)	
7. 3-(5-Methylfuryl)-N-furamidopropionamide ($C_{13}H_{14}N_2O_4$)	14. Indole (C_8H_7N)	

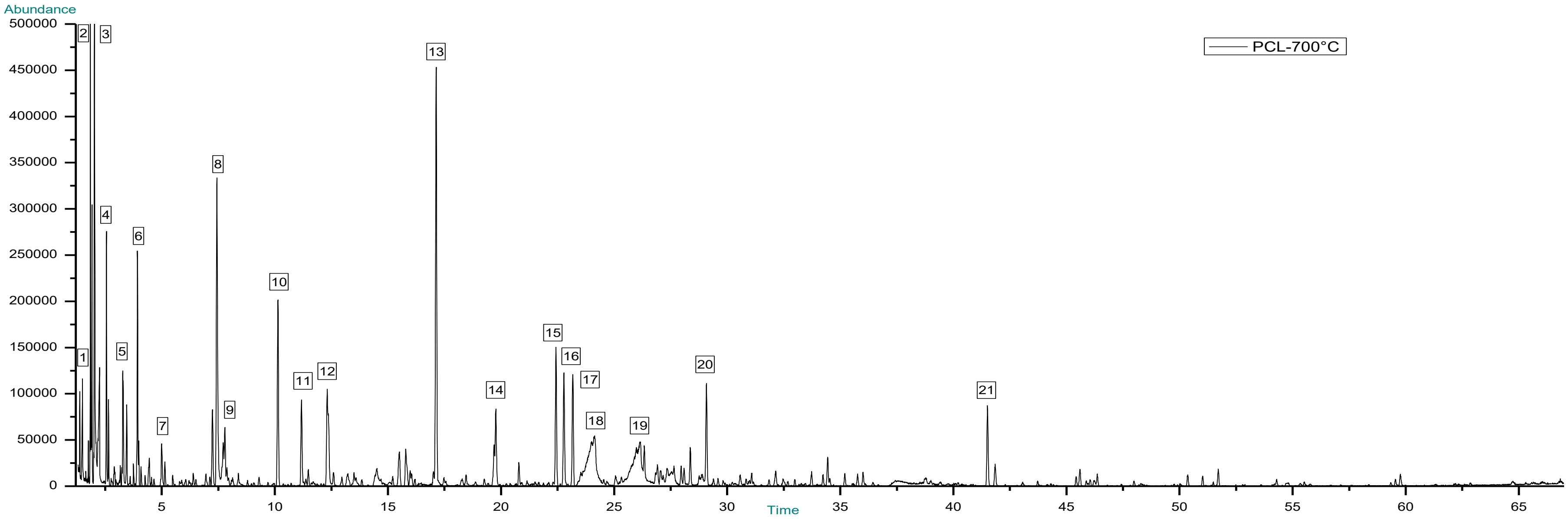


Table Compounds Identification of Oil from PCL 700°C.

Compounds Name	Compounds Name	Compounds Name
1. Benzene (C_6H_6)	8. Phenol (C_6H_6O)	15. Naphthalene, 2-methyl- ($C_{11}H_{10}$)
2. Pyridine (C_5H_5N)	9. Benzofuran (C_8H_6O)	16. Indole (C_8H_7N)
3. Toluene (C_7H_8)	10. Indene (C_9H_8)	17. Naphthalene, 1-methyl- ($C_{11}H_{10}$)
4. Pyridine, 2-methyl- (C_6H_7N)	11. Phenol, 2-methyl- (C_7H_8O)	18. 2,4-Imidazolidinedione, 5,5-dimethyl- ($C_5H_8N_2O_2$)
5. Pyridine, 3-methyl- (C_6H_7N)	12. Phenol, 4-methyl- (C_7H_8O)	19. 2,4-Imidazolidinedione, 5-methyl- ($C_4H_6N_2O_2$)
6. Styrene (C_8H_8)	13. Naphthalene ($C_{10}H_8$)	20. Fluorene ($C_{13}H_{10}$)
7. Pyridine, 3,5-dimethyl- (C_7H_9N)	14. Quinoline (C_9H_7N)	21. Phenanthrene ($C_{14}H_{10}$)

Appendix C

The proximate and ultimate tables of all the solid samples (feedstock and char) can be seen in appendix C, Table C.1 and C2. The ultimate analysis table is presented in as received, dry and dry ash free basis. The table of the liquid yield's water content, which was obtained by using the Karl fisher titration method can also be seen in appendix C (Table C.3).

Table C.1 Proximate analysis

Sample	Moisture (wt%)	VM (wt%)	Ash (wt%)	FC (wt%)
PCL	4.84	63.84	17.05	14.27
PCL Char 500°C	0.57	16.20	34.66	48.57
PCL Char 600°C	0.31	14.27	35.46	49.96
PCL Char 700°C	0.25	7.29	39.28	53.17
FCL	22.67	43.70	9.82	23.81
FCL Char 500°C	0.84	17.48	32.39	49.30
FCL Char 600°C	1.17	15.57	34.21	49.04
FCL Char 700°C	0.28	11.47	37.38	50.87
Hay Mix Char 350°C	2.72	43.07	29.47	24.74
Hay Mix Char 400°C	3.45	31.36	38.54	26.65
Hay Mix Char 450°C	1.57	31.18	36.36	30.89
Straw Mix Char 350°C	3.10	43.80	29.27	23.83
Straw Mix Char 400°C	3.54	32.62	37.59	26.25
Straw Mix Char 450°C	4.08	31.06	39.22	25.64
Rice husk Mix Char 350°C	2.98	44.65	34.45	17.93
Rice husk Mix Char 400°C	3.59	32.48	42.85	21.08
Rice husk Mix Char 450°C	3.78	30.07	44.15	22.00
Wood chip Mix Char 350°C	2.20	46.23	24.61	26.97
Wood chip Mix Char 400°C	3.80	34.22	34.58	27.40
Wood chip Mix Char 450°C	2.00	31.92	36.97	29.11

Table C.2 Ultimate analysis.

Sample	**As Received Basis**							**Dry Basis**						**Dry Ash Free**				
	C (wt%)	**H (wt%)**	**O (wt%)**	**N (wt%)**	**S (wt%)**	**Moisture (wt%)**	**Ash (wt%)**	**C (wt%)**	**H (wt%)**	**O (wt%)**	**N (wt%)**	**S (wt%)**	**Ash (wt%)**	**C (wt%)**	**H (wt%)**	**O (wt%)**	**N (wt%)**	**S (wt%)**
PCL	40.11	5.66	27.56	4.23	0.55	4.84	17.05	42.15	5.38	29.52	4.45	0.58	17.92	51.34	6.56	35.97	5.42	0.71
PCL Char 500°C	52.23	1.57	7.40	2.62	0.95	0.57	34.66	52.53	1.51	7.50	2.64	0.96	34.86	80.64	2.32	11.52	4.05	1.47
PCL Char 600°C	53.20	1.20	6.50	2.35	0.98	0.31	35.46	53.37	1.17	6.56	2.35	0.98	35.57	82.83	1.82	10.18	3.65	1.52
PCL Char 700°C	52.06	0.58	1.15	1.95	1.15	0.25	39.28	52.20	0.55	4.77	1.96	1.15	39.38	86.10	0.91	7.78	3.23	1.89
FCL	29.44	5.17	26.84	5.59	0.47	22.67	9.82	38.07	3.42	37.97	722	0.61	12.70	43.61	3.92	43.49	8.28	0.70
FCL Char 500°C	57.84	1.60	2.95	4.01	0.37	0.84	32.39	58.33	1.52	3.07	4.05	0.37	32.66	86.62	2.25	4.57	6.01	0.55
FCL Char 600°C	55.46	1.42	4.25	2.90	0.59	1.17	34.21	56.12	1.30	4.43	2.93	0.60	34.61	85.83	1.99	6.78	4.48	0.92
FCL Char 700°C	50.43	1.14	7.47	2.44	0.85	0.28	37.38	50.57	1.12	7.52	2.45	0.86	37.48	80.90	1.79	12.04	3.92	1.37
Hay Mix	34.50	5.47	29.14	3.60	0.27	10.32	16.17	38.41	4.81	33.67	4.03	0.30	18.78	47.44	5.88	40.79	5.46	0.43
Hay Mix Char 350°C	46.62	3.55	12.62	3.52	1.49	2.72	29.47	47.92	3.34	13.29	3.62	1.54	30.29	68.75	4.79	19.06	5.19	2.20
Hay Mix Char 400°C	49.33	1.50	5.42	1.65	0.25	3.45	38.54	51.09	1.16	5.87	1.70	0.26	39.92	85.03	1.93	9.76	2.84	0.44
Hay Mix Char 450°C	42.37	1.97	14.96	2.50	0.27	1.57	36.36	43.04	1.83	15.38	2.54	0.27	36.94	68.26	2.89	24.39	4.03	0.43
Straw Mix	32.15	5.35	33.71	2.89	0.30	9.81	15.80	35.61	4.70	38.36	3.25	0.33	17.75	44.03	5.71	45.18	4.63	0.46
Straw Mix Char 350°C	49.54	2.73	12.22	2.73	0.41	3.10	29.27	51.13	2.46	12.97	2.81	0.42	30.21	73.26	3.53	18.58	4.03	0.60
Straw Mix Char 400°C	50.53	1.58	6.55	1.44	0.20	3.54	37.59	52.38	1.23	5.72	1.49	0.21	38.97	85.83	2.02	9.37	2.44	0.35
Straw Mix Char 450°C	46.05	2.18	6.09	1.91	0.48	4.08	39.22	48.01	1.80	6.82	1.99	0.50	40.89	81.22	3.04	11.54	3.36	0.84
Rice husk Mix	32.05	4.86	27.60	2.85	0.31	10.28	22.06	35.69	4.14	31.95	3.21	0.35	24.66	47.46	5.51	41.92	4.62	0.49
Rice husk Mix Char 350°C	46.66	2.34	11.27	1.96	0.35	2.98	34.45	48.09	2.07	11.96	2.02	0.36	35.51	74.57	3.20	18.58	3.12	0.56
Rice husk Mix Char 400°C	44.93	1.46	5.82	1.21	0.14	3.59	42.85	46.60	1.10	6.45	1.26	0.15	44.45	83.89	1.98	11.61	2.26	0.27
Rice husk Mix Char 450°C	35.38	1.81	13.02	1.59	0.27	3.78	44.15	36.77	1.44	13.97	1.65	0.28	45.88	67.95	2.67	25.82	3.05	0.52
Wood chip Mix	35.77	5.68	31.43	2.81	0.27	9.95	14.09	39.62	5.06	35.96	3.17	0.31	15.89	47.31	5.95	41.78	4.53	0.43
Wood chip Mix Char 350°C	50.89	3.30	15.65	2.52	0.83	2.20	24.61	52.03	3.13	16.25	2.58	0.85	25.16	69.53	4.18	21.71	3.44	1.14
Wood chip Mix Char 400°C	48.68	1.43	10.09	1.26	0.17	3.80	34.58	50.60	1.05	10.93	1.31	0.17	35.95	78.99	1.64	17.06	2.04	0.27
Wood chip Mix Char 450°C	45.85	1.96	10.98	1.95	0.29	2.00	36.97	46.79	1.77	11.43	1.99	0.30	37.72	75.13	2.85	18.35	3.20	0.47

Table C.3 Water content (wt%) in pyrolytic oil from Karl fisher titration

Sample Name	Result 1(%)	Result 2(%)	Result 3(%)	AVERAGE (%)	SD
FCL Oil-700°C	81.09	83.56	82.41	82.35	1.009169
FCL Oil-600°C	69.14	72.15	71.39	70.89	1.278028
FCL Oil-500°C	73.3	68.68	70.39	70.79	1.907197
PCL Oil-700°C	77.65	78.6	78.24	78.16	0.391606
PCL Oil-600°C	70.5	73.01	71.64	71.72	1.026136
PCL Oil-500°C	71.69	73.64	75.2	73.51	1.435897
HAY MX-SP	62.6	62.55	61.85	62.33	0.342377
HAY MX-MP	63.53	62.76	63.1	63.13	0.315066
HAY MX-FP	63.39	67.18	68.04	66.20	2.020072
RICE HS MX-SP	71.53	71.7	71.24	71.49	0.189912
RICE HS MX-MP	72.28	71.9	72.03	72.07	0.157692
RICE HS MX-FP	76.42	76.37	75.81	76.20	0.276526
STRAW MX-SP	69.15	69.58	70.03	69.59	0.359289
STRAW MX-MP	73.94	71.99	72.56	72.83	0.818657
STRAW MX-FP	75.31	74.52	74.84	74.89	0.324448
WOOD SV MX-SP	65.12	65.94	66.28	65.78	0.486895
WOOD SV MX-MP	59.67	60.32	60.08	60.02	0.26837
WOOD SV MX-FP	55.44	56	55.23	55.56	0.324996

Appendix D

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) by using two types of feedstock namely PCL and char generated from heated PCL at the temperature between 400 – 600°C. The TGA process resulted in proximate data such as moisture content, ash content, fix carbon content and volatile matter content, whose table can be seen in the proximate test tables in appendix D (Table D.1). The graphic decomposition rate (dm/m0/dt (1/s)) towards the temperature elevation in the TGA process can also be seen in appendix D. The TGA for PCL was performed two times with samples that weighed 5 mg dan 10 mg. Meanwhile for all char, the TGA was performed one time with a sample that weighed 10 mg. The whole TGA process was conducted at TU Delft, the Netherlands.

Table D.1 Proximate Test from TGA

Sample	*Moisture Content (%)*	*Ash (%)*	*Fix Carbon (%)*	*Volatile (%)*
Poultry Litter (5 mg)	7.27	0.36	10.81	81.56
Poultry Litter (10 mg)	8.38	3.52	11.84	76.26
PL Char 400°C	3.41	14.99	32.93	48.68
PL Char 450°C	3.32	15.57	31.01	50.10
PL Char 500°C	3.25	17.62	28.86	50.27
PL Char 550°C	3.60	18.39	23.70	54.32
PL Char 600°C	2.92	25.06	16.39	55.64

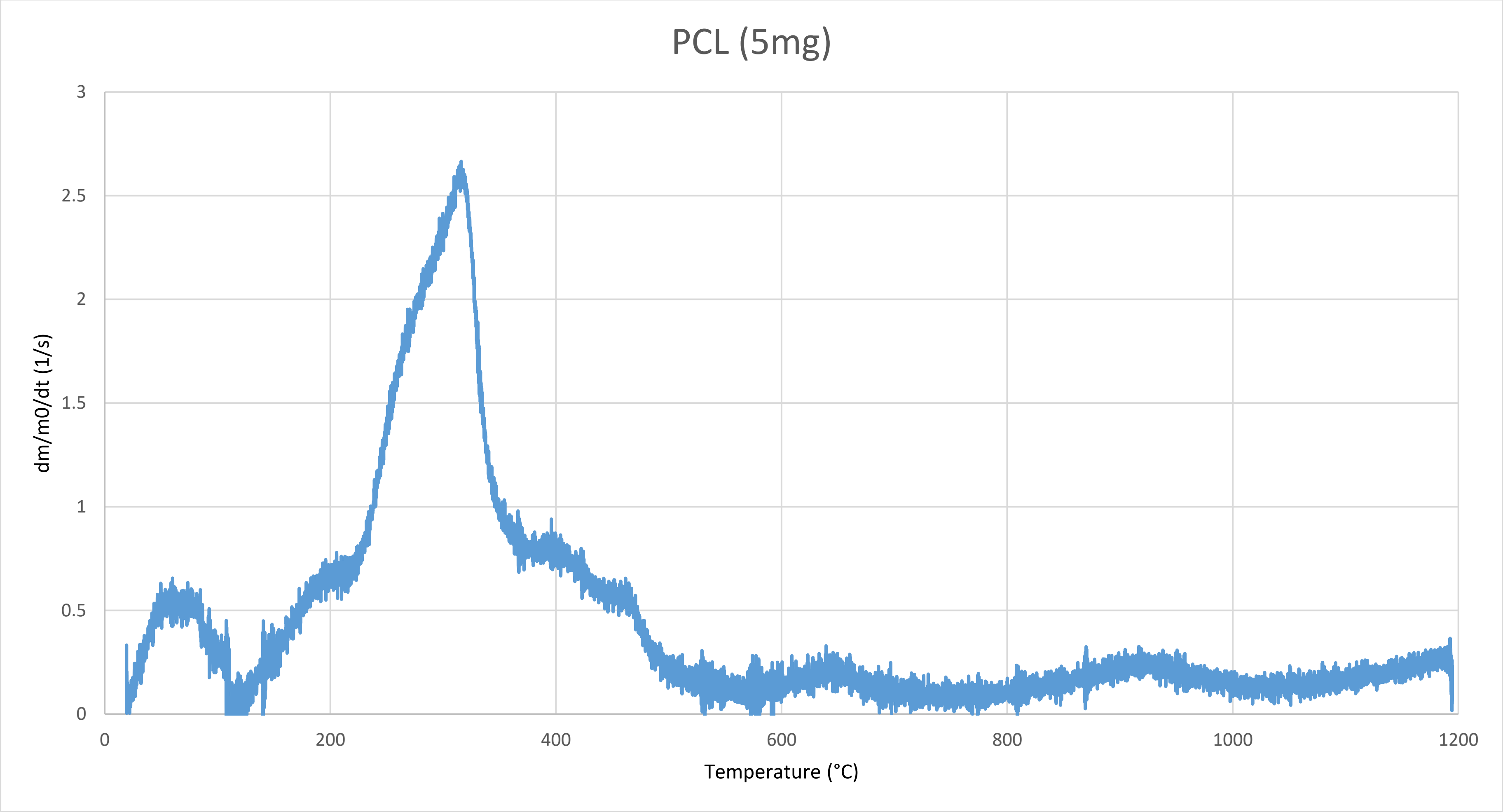


Fig D.1 Decomposition rate of PCL (5mg) in TGA

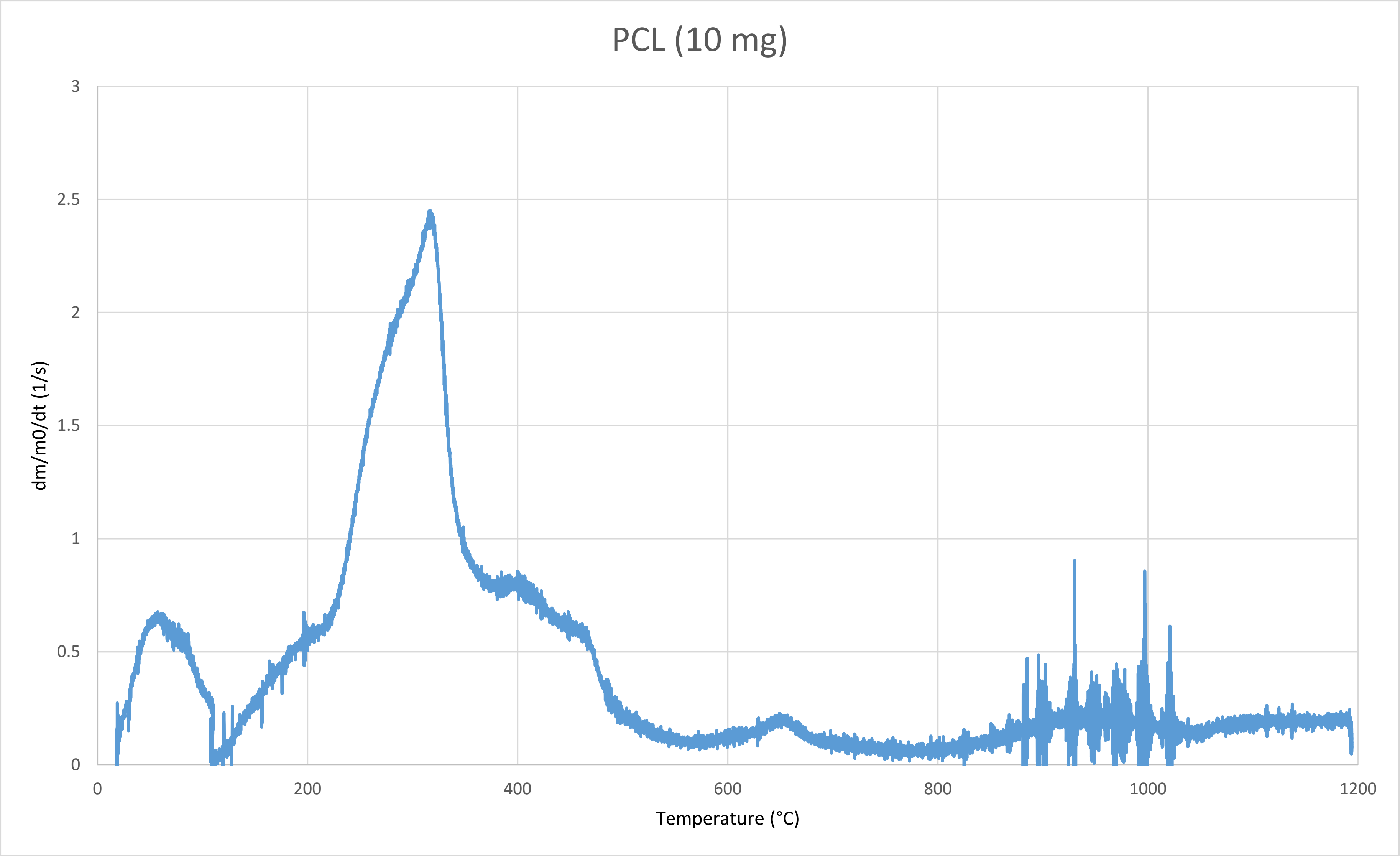


Fig D.2 Decomposition rate of PCL (10mg) in TGA

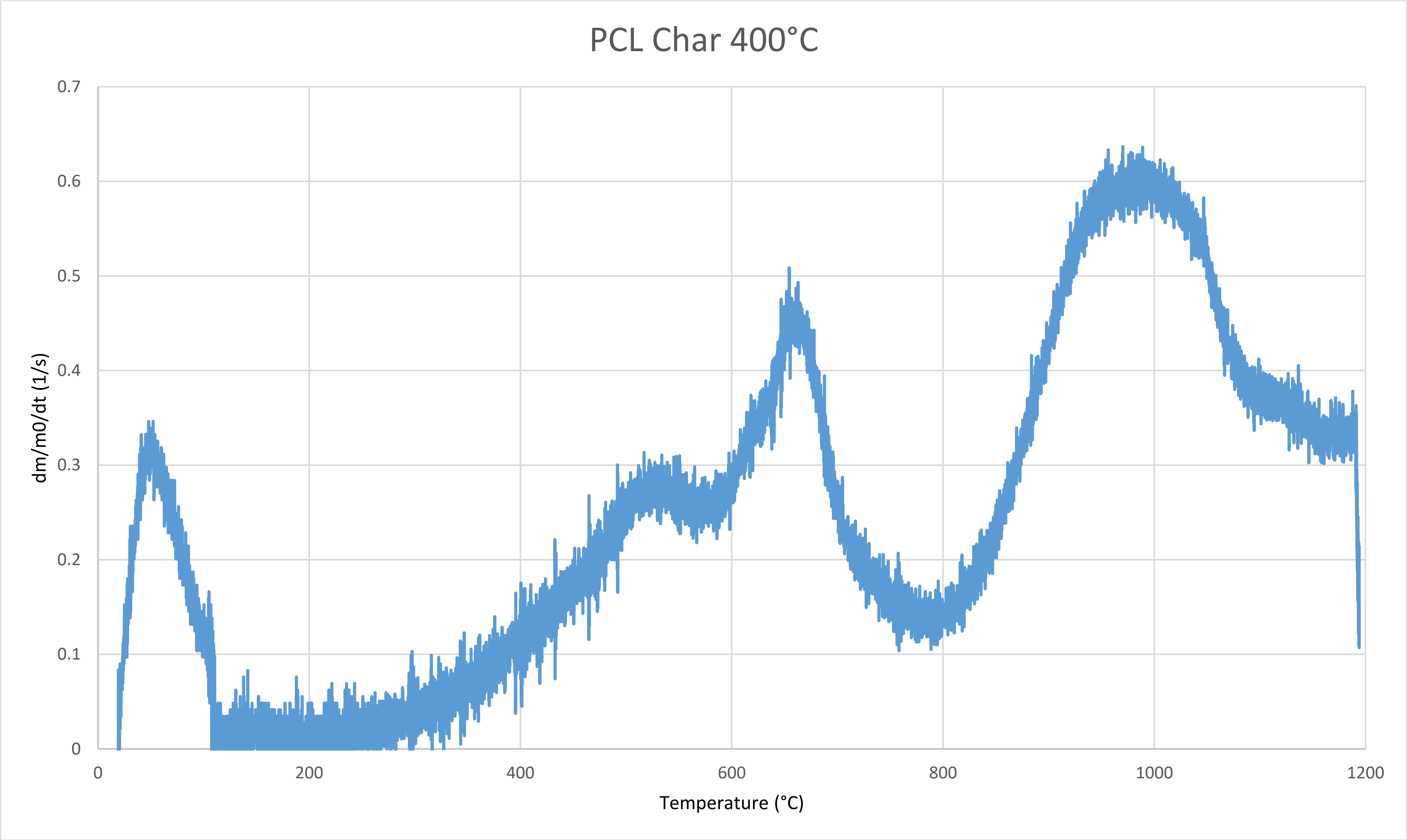


Fig D.3 Decomposition rate of PCL Char 400°C in TGA

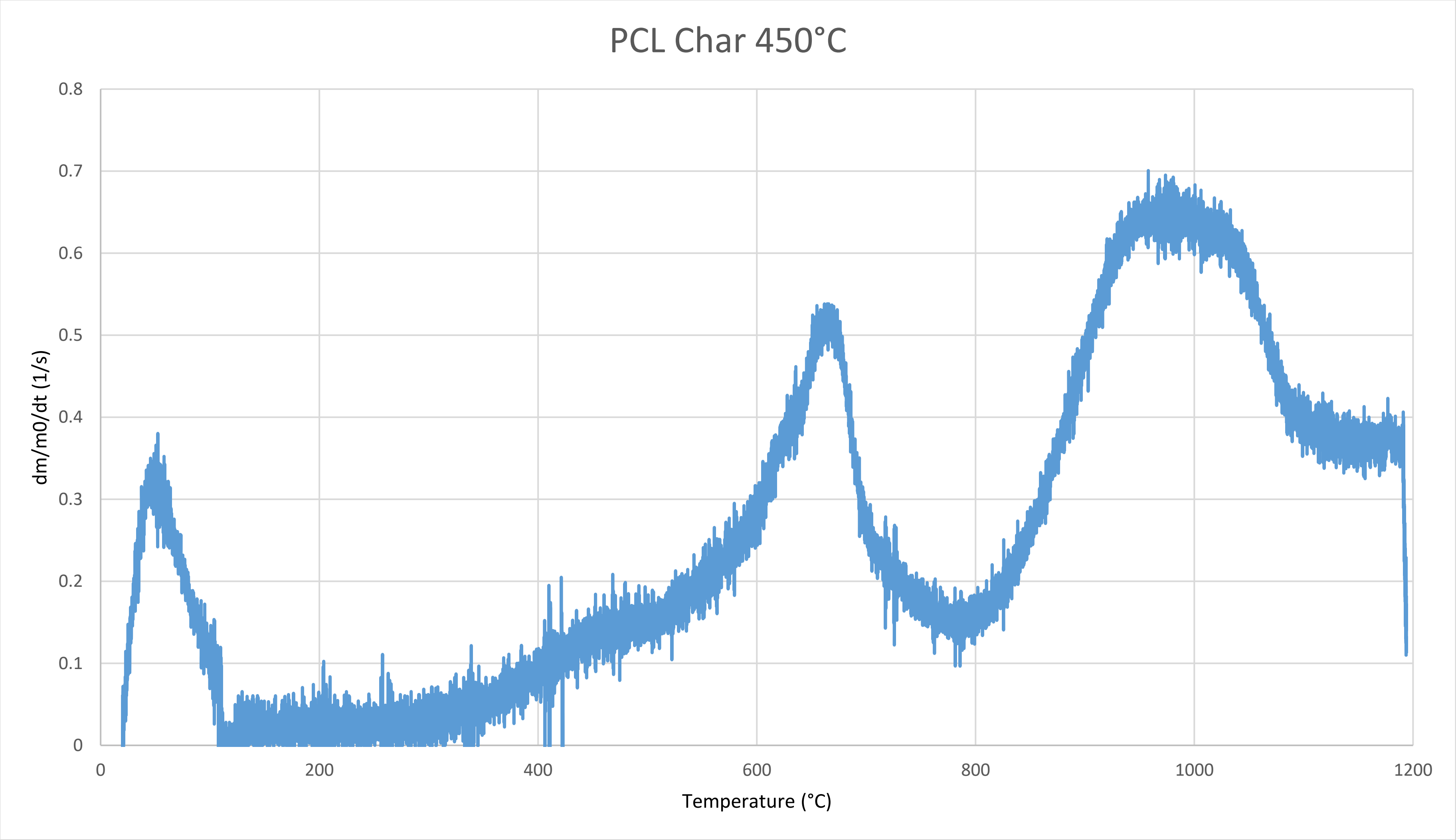


Fig D.4 Decomposition rate of PCL Char 450°C in TGA

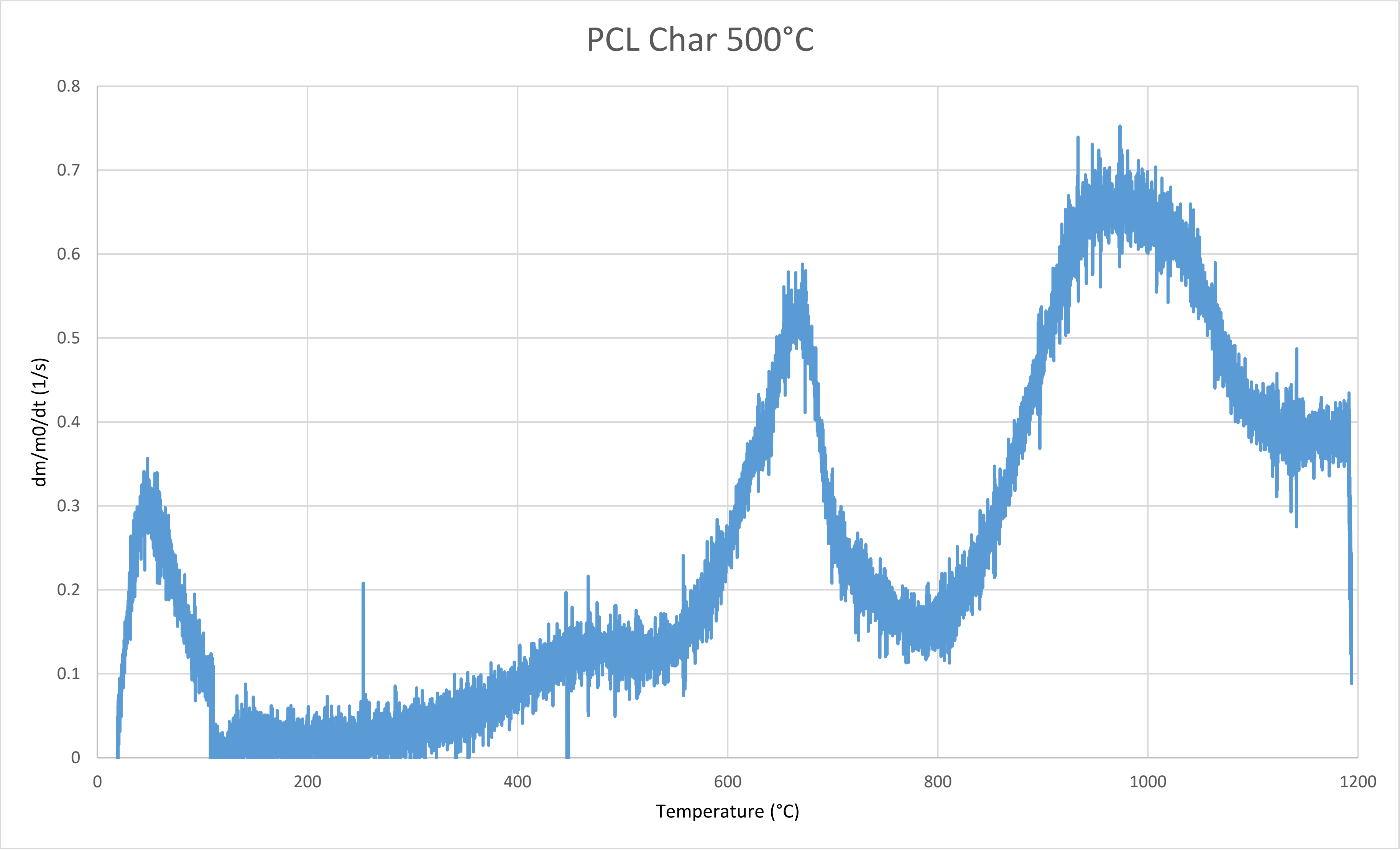


Fig D.5 Decomposition rate of PCL Char 500°C in TGA

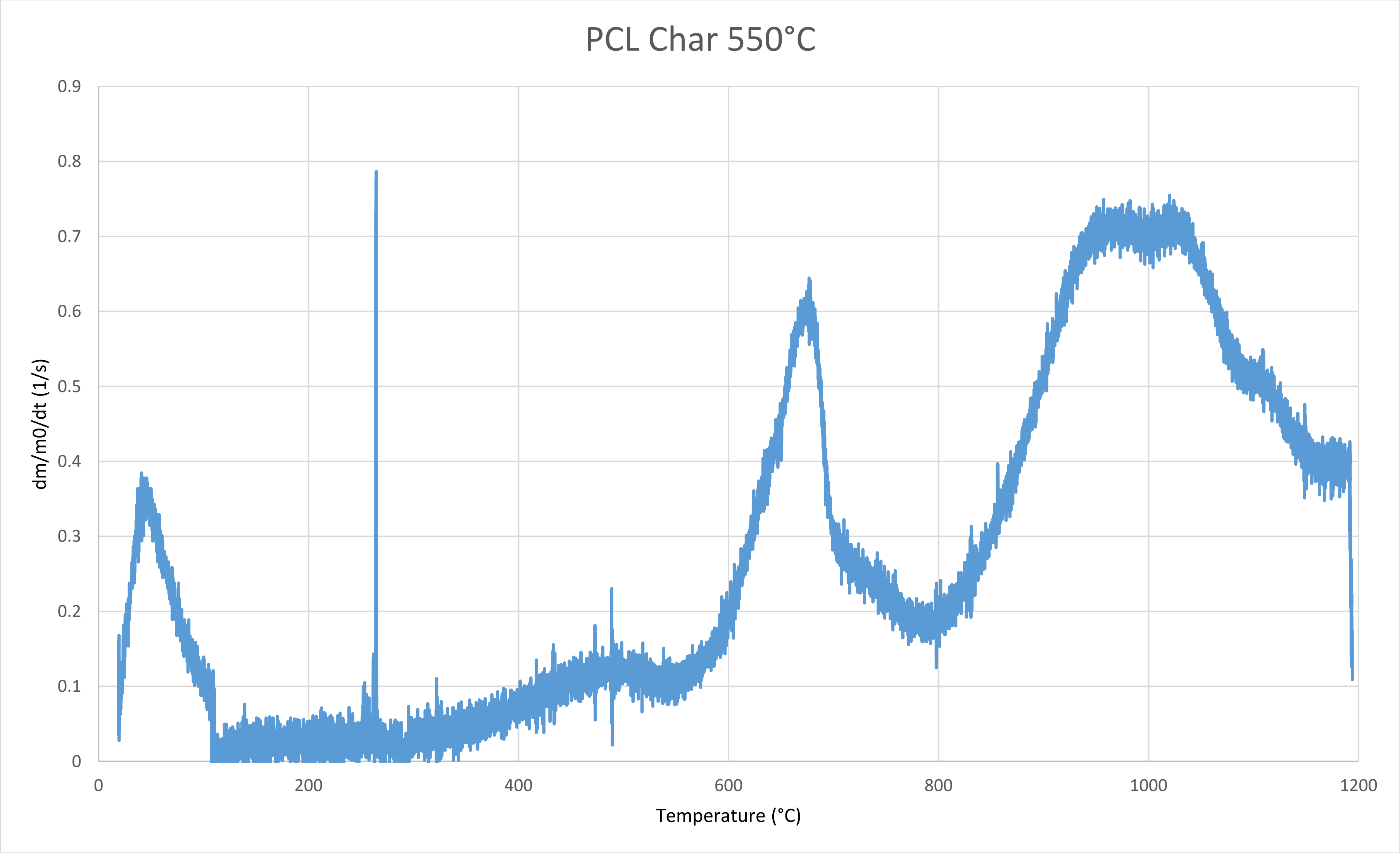


Fig D.6 Decomposition rate of PCL Char 550°C in TGA

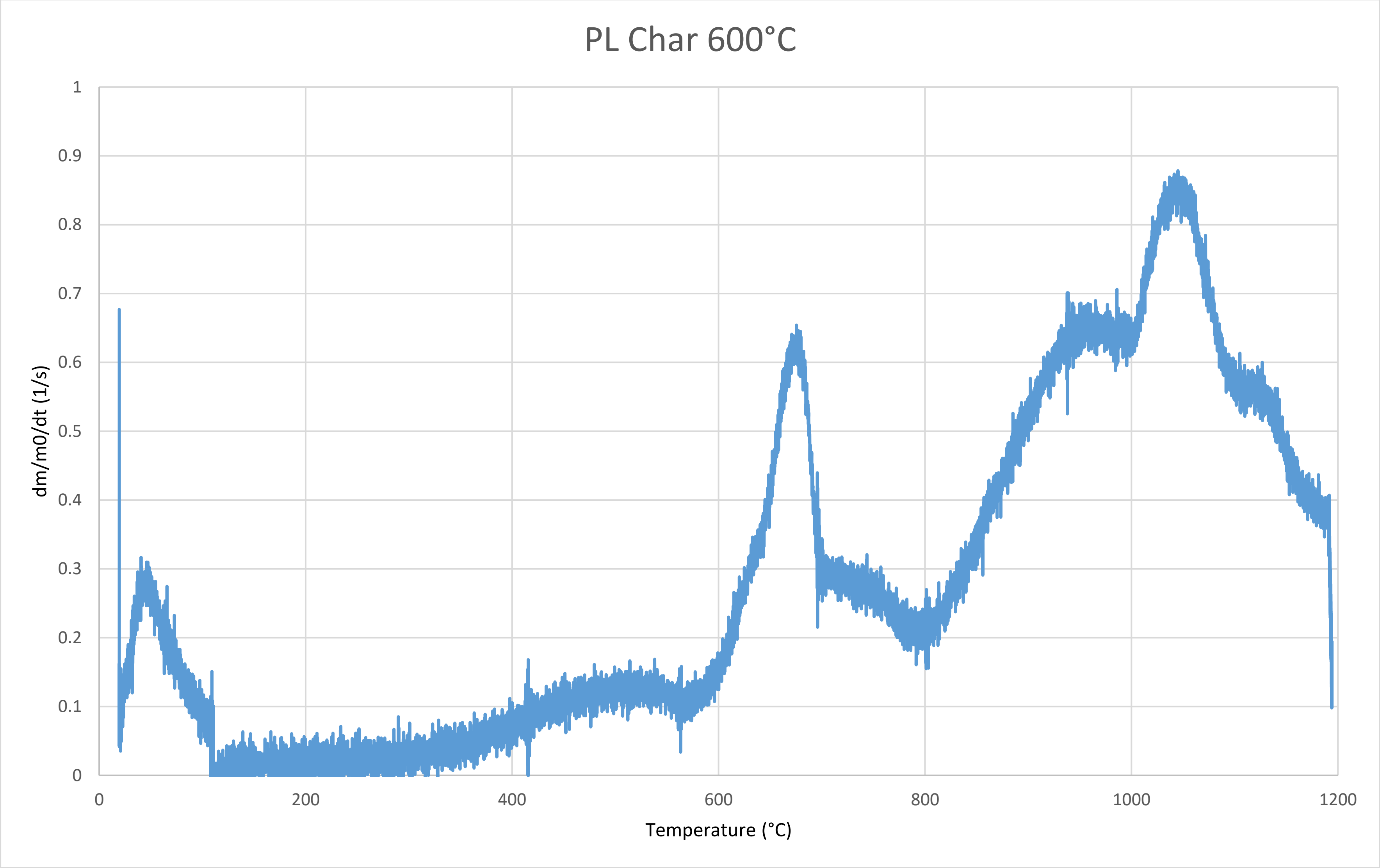
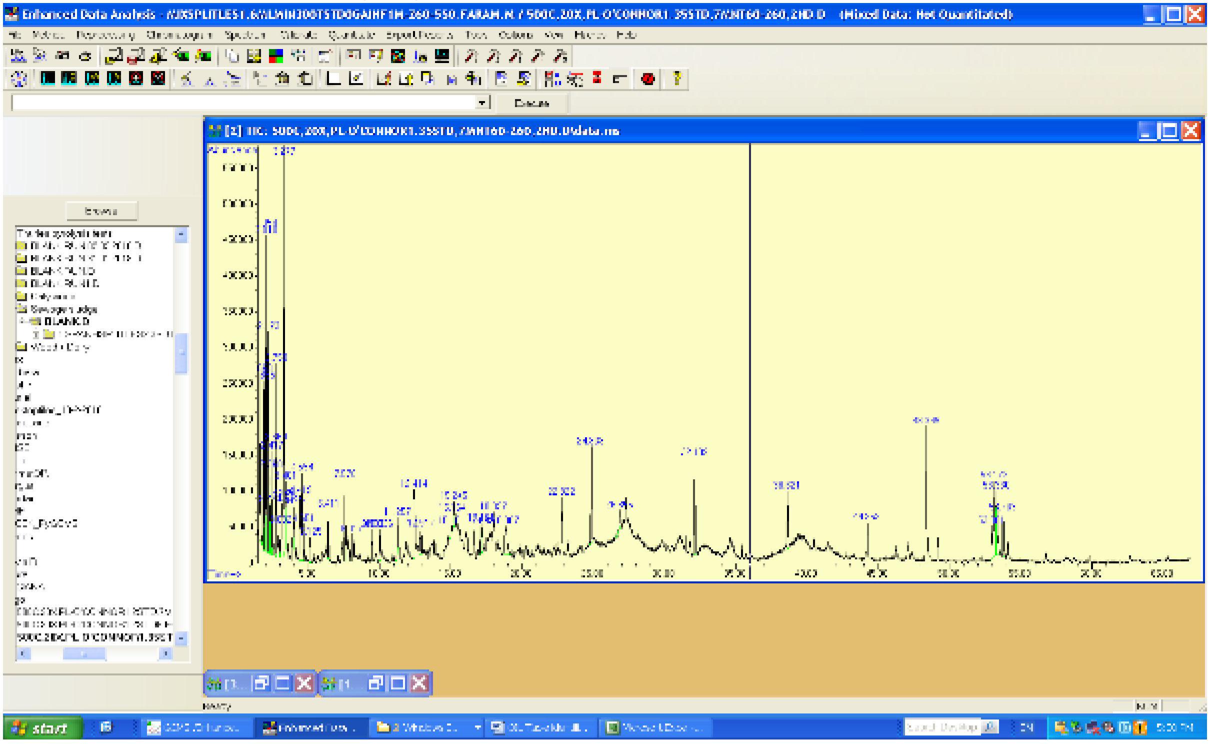


Fig D.7 Decomposition rate of PCL Char 600°C in TGA

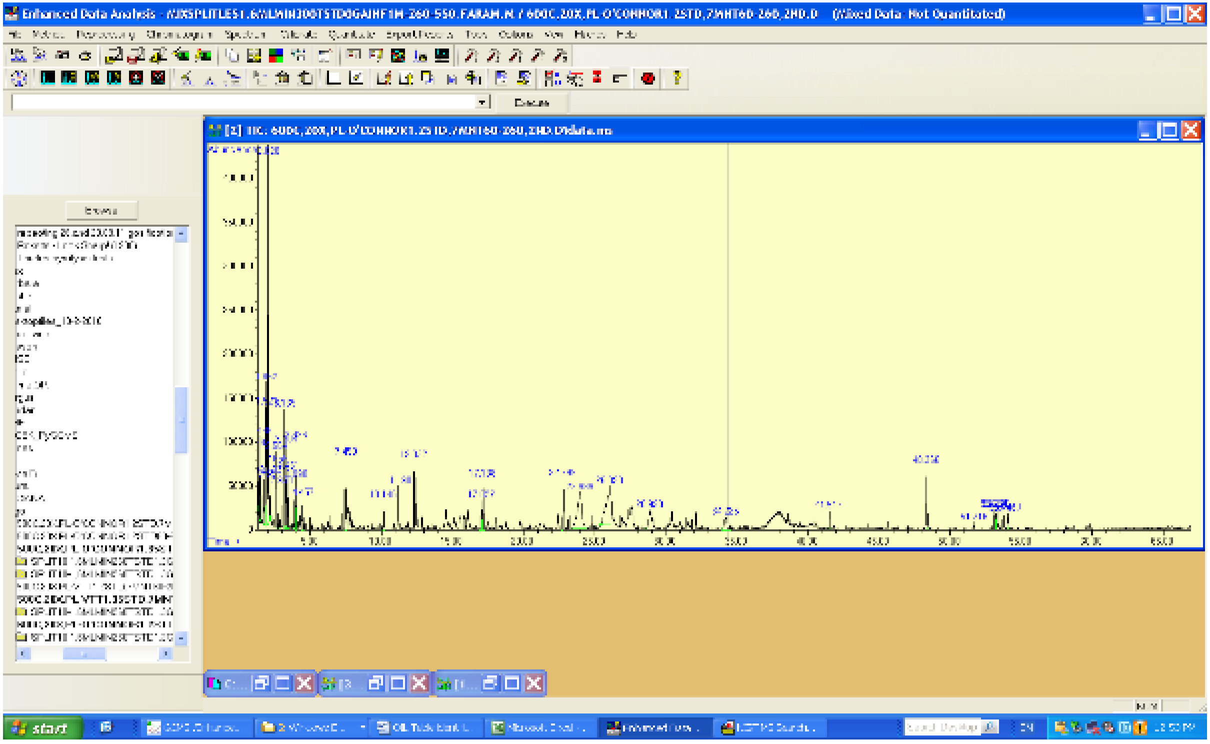
Appendix E

The quantification of the oil yield was based on the chromatogram result that can be found in appendix B. The peaks of the chromatogram were then integrated in order to obtain the area width. The area width was then used to obtain the concentration percentage of each compound identified in appendix B. The picture of the chromatogram integration can be found in appendix E. Due to the long storage time, oxidation reaction might happen in the oil yield from slow pyrolysis, this reason made the quantification of the oil yield was conducted only for the FCL and PCL intermediate pyrolysis performed at the University of Limerick.

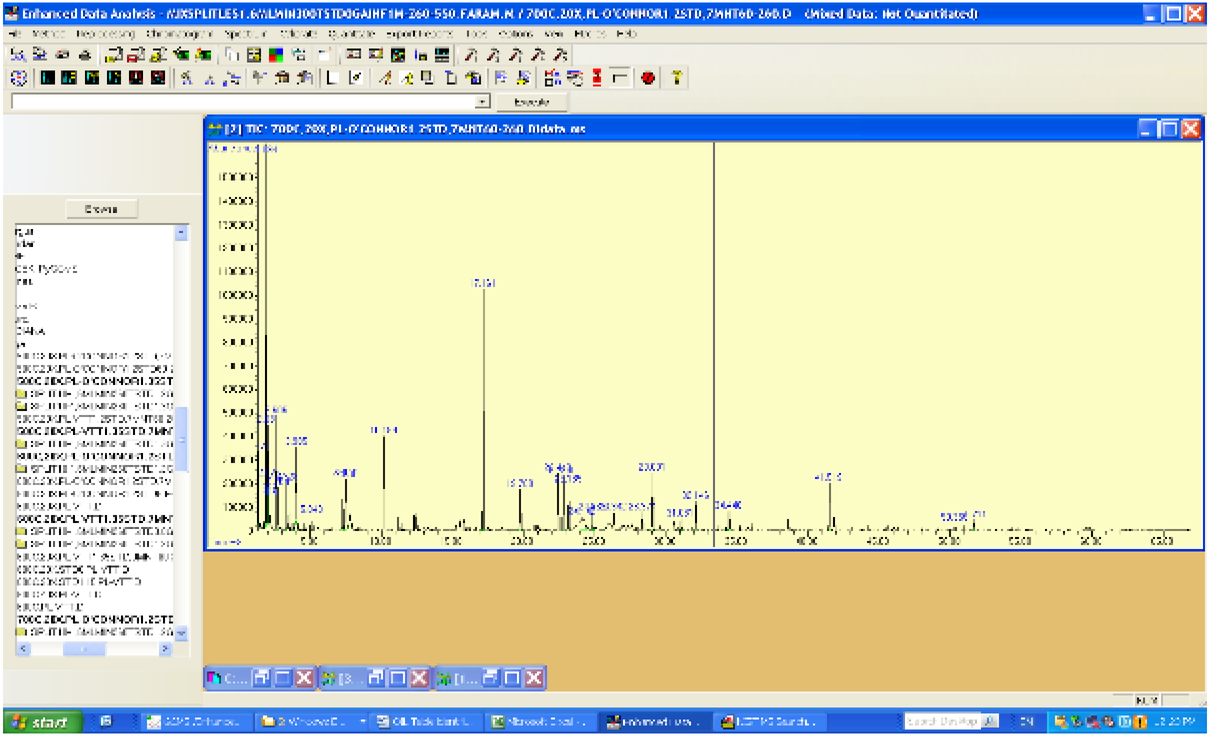
- Quantification oil from pyrolysis FCL 500°C:



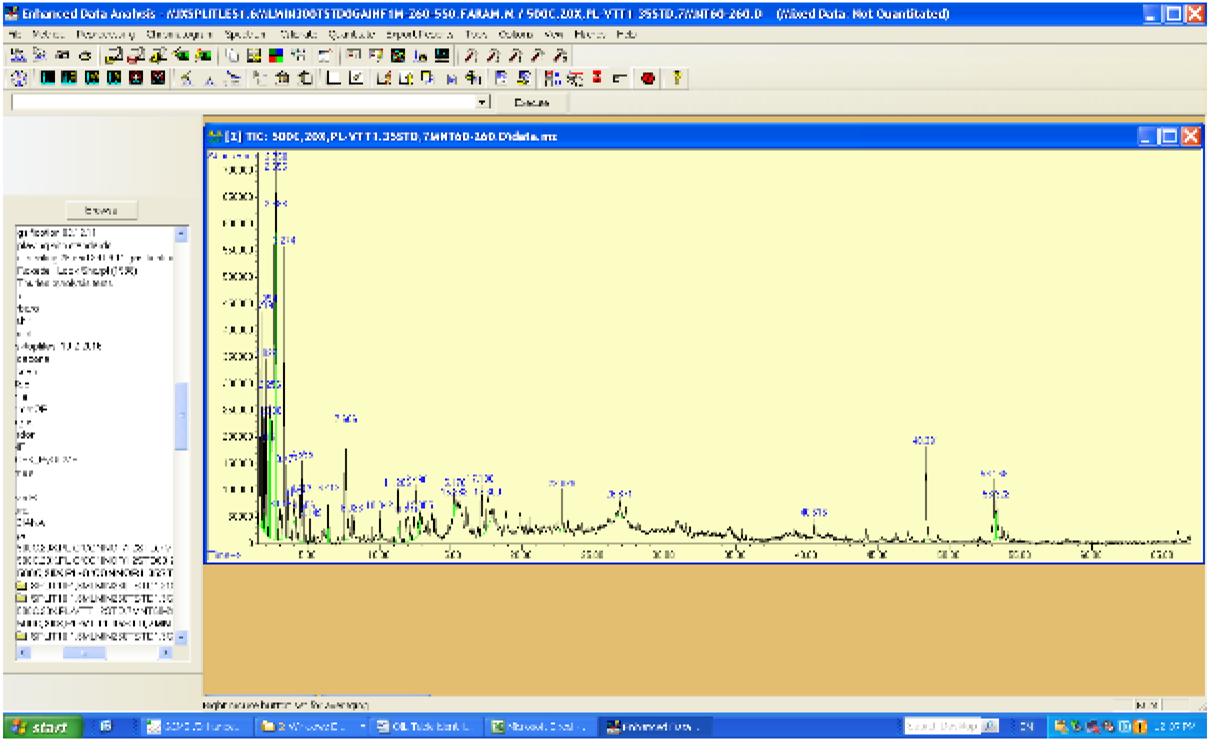
- Quantification oil from pyrolysis FCL 600°C:



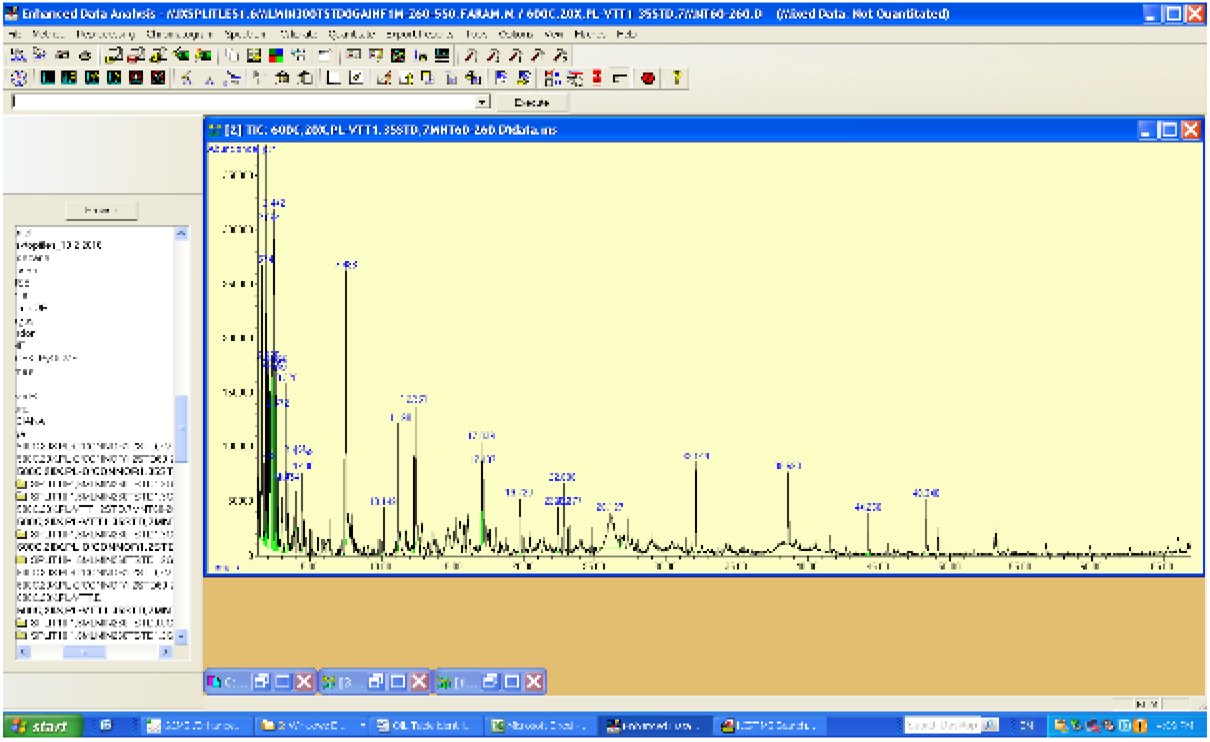
- Quantification oil from pyrolysis FCL 700°C:



- Quantification oil from pyrolysis PCL 500°C:



- Quantification oil from pyrolysis PCL 600°C:



- Quantification oil from pyrolysis PCL 700°C: