UNIVERSITY OF NOTTINGHAM

Can Date Pits Replace Crude Oil?

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The study of processing waste date pits into valorised extractables such as bio-oil using microwave methods and technologies to obtain high yields and phenolic extracts.

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List of Abbreviations Used

ABSL	Acetyl Bromide Soluble Lignin
C	Carbon
Cl	Chlorine
CO_2	Carbon dioxide
DMP	Dry Microwave Pyrolysis
DPC	Date Pit Core
DPS	Date Pit Skin
DPW	Date Pit Whole or Whole Date Pit
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
FC	Fixed Carbon
GC/MS	Gas Chromatography/Mass Spectrometry
GCV	Gross Calorific Value
GDP	Gross Domestic Product
H	Hydrogen
H_2O	Water
HHV	Higher Heating Value
HME	Hydrothermal Microwave Extraction
IL	Ionic Liquid(s)
KOH	Potassium Hydroxide
LC	Lignin Content
LHW	Liquid Hot Water
MJ/kg	Mega-Joules per kilogram
MT	Metric Tonne(s)
N	Nitrogen
O	Oxygen
Py-GC/MS	Pyrolysis GC/MS
S	Sulphur
TGA	Thermo-Gravimetric Analysis
USD	United States Dollar(s)
VM	Volatile Matter

Abstract

Date pits are an underutilised waste biomaterial, produced in large quantities in the Sultanate of Oman along with bulk date waste biomass and produce. As with most biomass, they have the potential to increase their value through traditional and novel methods and techniques. By breaking down the durable date pits into softer yields, they can open pathways for renewable biomass processing in the Sultanate and the region.

By reviewing the research performed on date pits; biomass as a whole and microwave interactions with date pits/biomass, a few points can be added to these specific areas by the research presented in this thesis. Especially with regards to bio-oil production via date pit valorisation and with regards to macroscopic microwave effects on biomass.

This thesis uses microwave methods to valorise date pits in a manner that would increase their calorific output as a potential solid fuel, soften them for mechanical and future processing and extract by-products that can be used as fuels or sources for platform chemicals. Using TGA, GC/MS and ABSL analytical methods, the date pit biomass potential has been observed and reported to compare the raw material and extracts appropriately based on their proximate data, higher heating values (as fuels) and degradation outputs.

Hydrothermal microwave pyrolysis managed to soften the date pits and liberate some of the lignin chains as a solid residue/powder; albeit in an insufficient and non-profitable quantity (0.6% of the date pits mass collected as lignin residue). The dry pyrolysis method quickly softened the date pits. It produced reasonable amounts of fermentable bio-oils while providing insight into microwave interactions with dry biomass and the mechanisms that induce fast pyrolysis and make bio-oil. The sequence of events leading up to bio-oil release from date pits and softening them by breaking down the hemicellulose chains is a critical contribution to future studies on renewable microwave practices.

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1. Introduction

Dates are a staple food in Middle Eastern and Northern African (MENA) regions of the world. Thousands of tons are produced and consumed annually by people and food industries globally, leading to a significant amount of waste biomass materials, including date-pit waste (Hossain et al., 2014). As the world moves toward a sustainable and renewables-reliant future, there is an excellent opportunity to develop methods to exploit the potential of a culturally relevant food source and its waste materials.

Being the largest crop produced in the Sultanate of Oman (> 50% of total agricultural produce), it is of little surprise that date farming produces more than 62000 tons of waste residues, which constitutes over 20% of the annual production weight (Abu-Jrai et al., 2017). Aside from the fruit, the various parts of the tree such as the pits/seeds and trunk contribute to a significant amount of wasted biomass (Zafar, 2016). The trunk, like most woody agricultural waste is burnt as fuel or composted as fertilizer. The seeds however, find little use aside from replanting more trees with no guarantee all seeds will germinate and reach maturity, thus leaving over 30000 tons to be discarded. In the United States, they have been used as road base gravel (Hamada et al., 2002). The seeds have also been used by farmers as animal feed or supplement for broiler diets (Hussein et al., 1998). Researchers in the Sultanate of Oman have recently explored a string of uses for date pits in biodiesel production, from extraction of bio-oil (10 – 15% yield) to catalysis (KOH impregnated carbonised date pits) and combustion (transesterified bio-diesel with a calorific value of 43.24 MJ/kg) (Jamil et al., 2016; Abu-Jrai et al., 2017; Hellier et al., 2019). Date pit bio-diesel is reported to be inherently clean, with practically no sulphur content and comparable to normal diesel fuels in terms of energy output (43.24 MJ/kg vs. 45.5 MJ/kg respectively).

Aside from the opportunities of date pit biomass, there is also the matter of the date pit hardness that requires mechanical processing before it is used for other purposes. Including the studies mentioned previously, few sources have examined whole (unground) date pits as a feedstock rather than crushed powder, as their natural hardness and bulk density can be a hindrance to chemical processing by inhibiting access to the internal lignocellulosic structure. Since the internal components cannot be accessed through conventional means, energy intensive crushing remains the current process route for date pits and other similar hard biomass feedstocks. Studying ways to soften hard biomass while obtaining valuable product streams would benefit the industry greatly by removing a costly and energy draining step in the process. By eliminating this step, a more streamlined and commercial process chain can be designed from source to profit while taking away the need to crush a hard waste material and turning it into softer, more useful energy and food substances.

One of the main issues driving the current Omani economy is pushing towards more sustainable renewable energy and resource industries. Due to rising prices of fossil fuels and their expected depletion in the relatively near future, the need for cheap, accessible and preferably renewable energy technologies increases. Multiple studies are being conducted, researching methods to expand upon renewable resource generation and usage from waste materials and steer the world from quickly depleting such valuable and limited resources as petroleum. Some research focused on limiting or recycling the waste produced from other industries such as bio-waste from agriculture.

The researcher’s home country, the Sultanate of Oman, has heavily relied on the fossil fuel industry as its economic backbone, as well as providing many advantages and subsidies to the citizens. Although this has greatly benefited the country in terms of establishing infrastructure, it is clear it is not a sustainable approach toward future energy and economic development. This is not only due to dependence on a non-renewable resource, but also due to the instability and fragility of the petroleum market. This was made especially evident twice within the last decade alone, during the 2016 oil crisis and COVID-19 pandemic (Kalantari & Sergie, 2016; Carrington et al., 2020). These events have illuminated the need for a renewable energy and materials industry in the Arabian Gulf to supplement the current industry, as well as support and drive the economy in times of difficulty. Oman and the Middle East may not have a reliable bio-industry but by implementing some of the suggested methods and technologies in the energy infrastructure, alongside a high demand and growing representative food sources, they can benefit economically as well as environmentally. With jobs on the line as well as subsidies being reduced, the inherent lifestyle that many Omanis of the current generation are accustomed to may drastically change for the worse as necessities become more expensive with every major oil price slump. Replacing or supplementing the oil economy with a bio-renewables economy for chemical and fuel sourcing, alongside solar and geothermal energy supplying the national electricity grid, can help feed a growing population figuratively and literally with date palm as a basis/symbol for development and growth.

This research thesis will revolve around the examination of the date pit as a potential feedstock for biomass processing, with the help of studies conducted on composition of the biomass resource and comparison of methods to harness the potential present in date pits. This study expects to optimise a methodology that will ignore the natural hardness of date pits, is also environmentally benign while adding value to waste date palm biomass by extraction of valuable products such as lignin and bio-oils/diesel. With lignin in particular being a potential compact and cheap source of phenolic and aromatic chemicals that can be used to supplement industrial fuels as renewable specialty products that can enhance the current Omani petroleum industry. As well as adding a carbon neutral step in the fuel economy of Oman, by potentially lowering the need for non-renewable sourcing of hydrocarbons and obtaining them from local biomass wastes.

For this study, two methods will be used to process the materials with consideration to the natural environs of Oman being extremely humid and ample coastal water supply or dry and arid desert: Hydrothermal Microwave Extraction and Dry Microwave Pyrolysis. More reasons for choosing these methods will be explained below in section 2.5.

The expectations for this thesis is to determine a methodology that can add value to date pits by obtaining beneficial yields and making them more desirable and processable. The goal of this research is to establish a valid pathway to process date pits. As can be seen in Figure 1.1, optimally valorising date pits can provide resources and opportunities to the local Omani community. By taking advantage of agricultural and consumer waste, processing them through different biorefinery methods, the generated valorised products can be used to better the Omani lifestyle by providing a less volatile source of fuel and income. The waste generated downstream can then be returned to the biorefinery to be reprocessed or to the farms as safe and biodegradable agricultural enrichers. This will be determined through extensive literature review and experimentation to show the qualitative results of processing date pits under microwave conditions; what can be done with the subsequent products and what benefits they give to the energy and materials platforms of the Middle East.

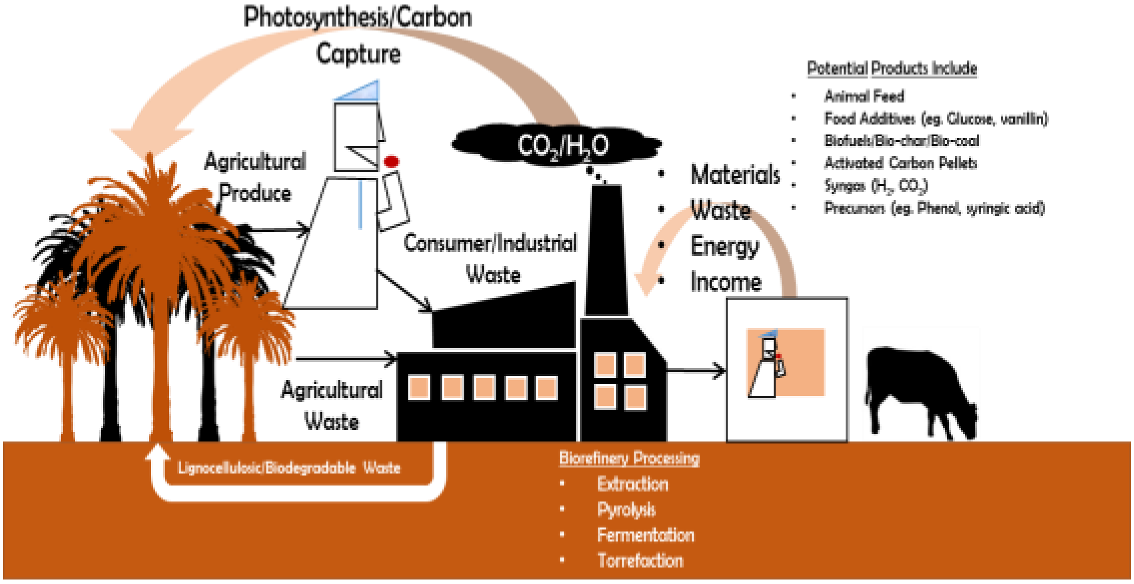

Figure 1.1 A conceptualised expectation of applying date pits to a biorefinery setting in the Sultanate of Oman.

1.1. Problem Statement

Date pits have the potential to be a good and sustainable source of platform chemicals, despite the large amounts of date palm waste generated; however, they have been generally underutilised as a biomass resource and, due to their natural hardness, must overcome a hurdle to be ground before processed via many current methodologies.

1.2. Aims & Objectives

The aim of this PhD research was to understand potential processing routes for the valorisation of date pits in a biorefinery, with a specific focus on lignin-rich products. The objectives were:

- Understand the physical and chemical characteristics of date pits in order to identify potential valuable products,
- Identify and develop processing routes that maximise the production of lignin and reduce or eliminate the need to grind the date pits,
- Assess the performance of those processing routes in terms of yield and composition of valuable components, as well as impact on the grindability of the residual date pits for further valorisation.
- Based on the characterisations and yields obtained; determine if date pits are a viable replacement for conventional fuels and platform chemical sourcing (crude oil and charcoal).

The objectives of this research thesis will involve the following steps:

- Characterisation of date pits as a viable waste biomass resource/feedstock in terms of: phenolic content represented as lignin; energy content obtained from proximate and thermal analysis; processability/grindability using point load measures for initial breaking force and dielectric analysis to design microwave based biomass processing methods.
- Observe and analyse the yields obtained from the hydrothermal microwave treatment of Omani date pits. Examining the solid extracts with respect to energy content, lignin/phenolic yield, purity, bulk economic yield and benefits. As well as the mechanical processability of the processed date pit husks.
- Observe the behaviour and yields of the Omani date pits under direct microwave radiation during dry pyrolysis. Examining the observable microwave effects that occur under different physical conditions of the date pits and the quality of yields obtained, for comparison to the yields obtained via the hydrothermal method.

In regards to the potential products of date pit biomass, three have been focused on in this work:

- Lignin/phenolic based solid material, which is worth upward of $650/ton based on purity and can reach as high $6500/ton (Guzman, 2020). It is also a prime platform polymer that leads into a whole phenol industry useful for phenolic fuel additives or medicines (as suggested in a lengthy study by Vinardell and Mitjans (2017)).
- Date pit charred husks (residue), which can be carbonised or highly purified cellulose/sugar and softened, which can then be used as a source of sugar for food; a processed high energy animal feed or as a carbon pellet which can then be activated for alternative uses such as water purification and desalination.
- Bio-oil extracts which can be then used as a fuel additive; a fermentable source of bio-ethanol depending on the contents or converted into bio-diesel, to compete with petroleum as a fuel alternative for the local populace.

2. Literature Review

2.1. Date Palm

Date fruits contain a significant amount of sugars and dietary fibres, and have been studied for their nutritional benefits. With the date pits weighing around 15% of the dates mass on average (Hussein et al., 1998), and more than 8 million tons of dates being produced per year globally (FAO, 2017), in addition to date pits being a major waste component (as they are generally inedible by humans), it is estimated that at least 1.2 million tons of date pits are produced annually.

Phoenix dactylifera, the species of plant known as date palm, has a long history of cultivation and is a cultural symbol due to its significance and presence as a staple food. There are multiple varieties produced throughout the globe, with most variation present in the MENA region, the primary region of world date exports. Popular varieties include Medjool found in Morocco and Deglet Noor from Algeria, with many more varieties bred to enhance their flavour and texture using modern agricultural methods as they become more accessible and affordable in the arid regions (Al-Yahyai & Khan, 2015).

The Sultanate of Oman produces more than 350,000 MT per annum of fruits (FAO, 2017) from more than seven million trees (Al-Yahyai & Khan, 2015). While half of the harvest generally goes toward human consumption in its various products, the remainder is discarded as animal feed or spoiled surplus/waste. This is not including the remaining parts (such as the bark and leaves) that are burned or composted as excess fertiliser during growth and harvest. These then add to landfills which already contain potentially biodegradable waste that is not studied as part of this thesis. Though there have been studies that indicate portions of date fruit (and thus, their seeds) are lost during harvest (Al-Yahyai, 2007; Manickasavasagan et al., 2013), this research thesis aims to find ways to utilise the waste as feedstock for added value products, with the standpoint that processing "harder" biomass (seeds) can pave the path to process "softer" biomass (vegetation and waste) more effectively.

2.2. Natural Contents

The nutritional capability of date pits has been considered. One study has found that date pits may contain bioactive components extremely beneficial for consumption (Hamada et al., 2002). The date pits have been observed to contain dietary fibres, which can be added to other foods to enhance digestibility. Analysis of the carbohydrates within the pits shows that they are primarily divided between the dietary fibres and phenolics, including cellulose and lignin, at relatively high concentrations (32.77% and 37.03% respectively, after accounting for extractives) if extracted efficiently (Nasser et al., 2016). Most of these fibres are insoluble in water and can be processed further into beneficial compounds (Al-Farsi & Lee, 2008). According to Al-Farsi & Lee, the phenolic analysis shows a high concentration of Protocatechuic acid (Figure 2.1), which may be broken down and reconstituted into useful materials and medicines such as phenol or flavonoids (2008). Examples of nutritional uses of date pits include usage as a flour alternative (Wahini, 2016).

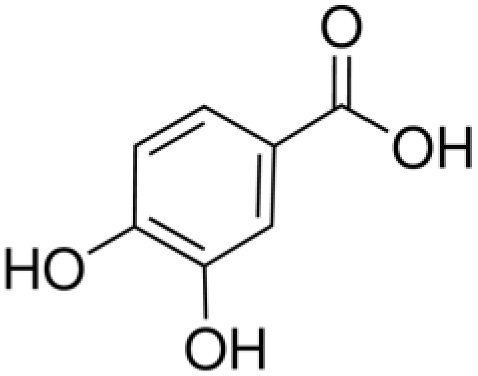

Figure 2.1 Protocatechuic Acid. A phenolic that is present in many healthy foods such as dates and green tea. Note the benzene ring, a component found commonly in crude oil products.

The phenolic content of date pits should also be addressed. Though there would be a significant amount of lignin in the palm tree fibres from agricultural waste, the emphasis here is on the primary source of domestic waste, the date pits. Data provided by Hossain et al. shows a similarity in content between the fruit and pits (2014). The phenolic content within the date pits is low in any single date pit, with concentrations ranging from 6 to 18 g/100g, depending on many factors (such as cultivar, environment and soil) (Al-Farsi & Lee, 2008). Considering the mass of dates pits, many useful platform chemicals can be obtained instead of being discarded in landfills.

Lignin is the primary source of phenolics in most plants; its original function is to help form cell walls and assist in maintaining the rigidity of plant structures. Lower in abundance than cellulose, which shares its functionality in maintaining plant structures, lignin is predominantly insoluble in water and is theorised to help transport water within the plant. It is also a beneficial fertiliser in nature, as plants die and biodegrade into soil and flora surrounding dead plants (Baurhoo et al., 2008; Zhang et al., 2013).

Aside from its natural uses, studies have shown that lignin can provide significant economic benefits for the renewable energy and materials industries. Research in 2013 was conducted to see if lignin can be used as a cheap and environmentally friendly alternative for generating bioethanol and phenolics, which in turn can be used to generate electrical energy and power (Pourhashem et al., 2013). Another study has shown that lignin can also be used and converted into other useful organic chemicals and materials (Northey, 1995). Due to its organic composition (Figure 2.2) and large polymeric structure, lignin-based products can either be burned as fuels or converted into smaller organic and manageable polymers. Lignin can also produce carbon fibre-based products, such as wind turbine blades (Kessler & Maiers, 2012), building up and helping other renewable energies flourish.

Lignins structure (as seen in Figure 2.2) comprises of many complex organic structures and polymers chained together, forming long phenolic chains high in aromatic content. The composition of lignins varies as much as there are species of plants and components (such as stem; roots and seeds) of each plant. It has potential to generate biofuels from renewable and abundant resources such as waste plant material from gardens, farms and foods (Welker et al., 2015).

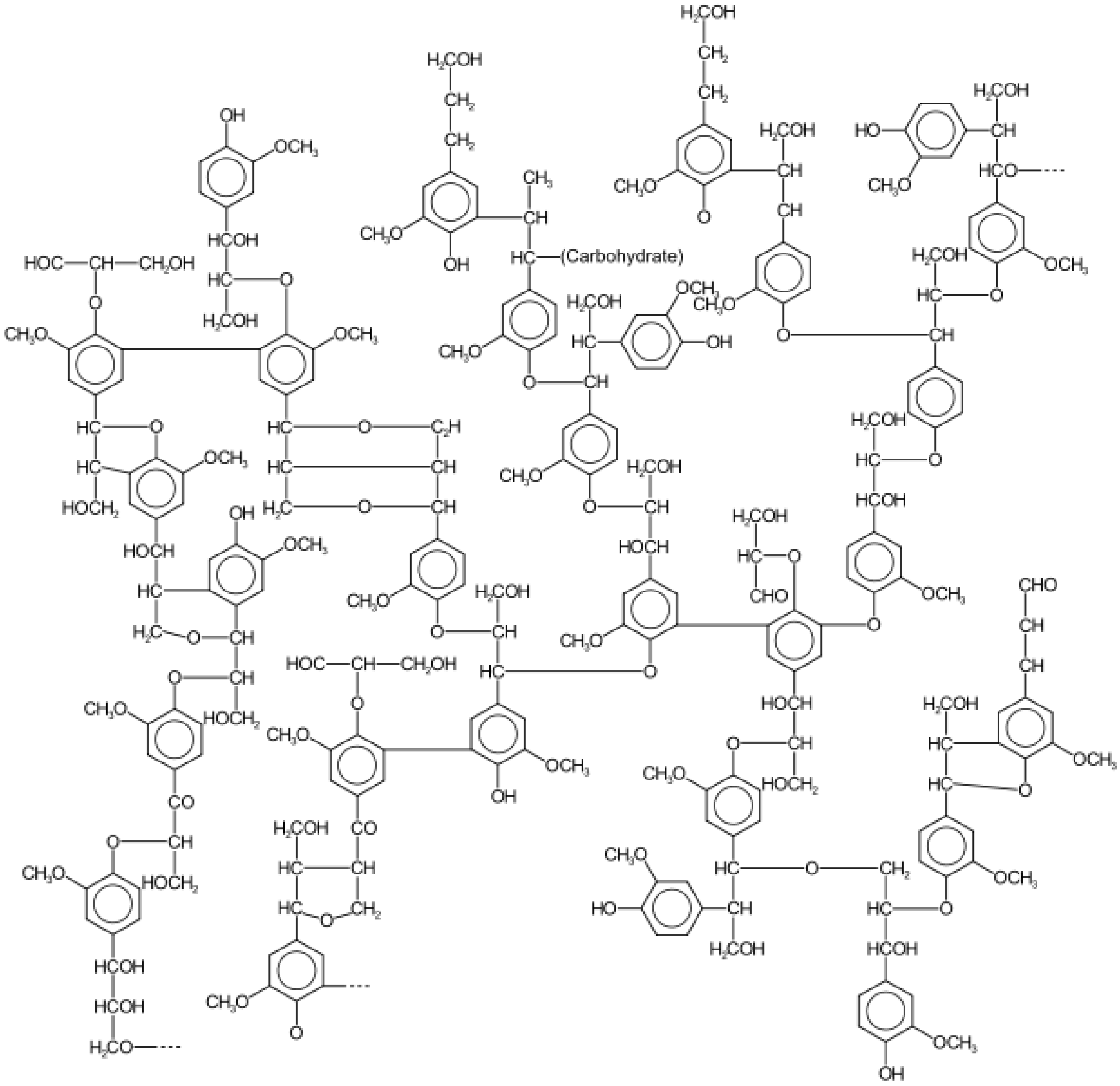

Figure 2.2 An example of lignin polymer in one of its many possible configurations (Glazer & Nikaido, 1995). The overall structure can vary greatly depending on the biomass source (Mahmood et al., 2018).

Studies are also currently being conducted into extraction methods of lignin and other phenolic compounds from these renewable sources, ranging from chemical-based conventional methods to newer technology-based methods. Methods such as alkaline and acid pre-treatments have proven to work with varying results and have been thoroughly researched (Nuruddin et al., 2014). Although the main drawback is that chemical-based extraction is a generally slow process, and is potentially toxic to surrounding environs.

2.3. Opportunities & Challenges in Using Date Waste

Aside from being consumed, date flesh may be rejected by farmers with remnants of unripe/overripe food and returned to the soil to eventually degrade, or may be discarded by consumers in developing countries as waste for landfills. The date pit however may go on to seeding further resources, or used as fertilizer, or highly nutritious animal feed in broilers, noted for enhancing the growth performance in chickens (Hussein et al., 1998). The final and common alternative is that date pits may be discarded and treated as consumer waste. It is reported that in Tunisia, 1000 tons of potential date seed oil is discarded annually due to date waste accumulating during growth and collection, and classified as not edible (Chandrasekaran & Bahkali, 2013). The waste is easy enough to collect from farms and commercial institutions but the challenges lie in implementation of valorisation processes; especially processes that would eliminate the grinding steps for hard biomass such as date pits or enhance the thermal output and calorific content of the date pit biomass.

What if dates could be used for more? Research has been conducted to extract high value chemicals from date pits, as well as to develop sustainable resourcing of pyrolysis bio-oil and char from waste date biomass, the proximate analysis data provided by this study has found raw date pit to produce a higher heating value of 18.9 MJ/kg when burnt, in comparison to dry wood at 16.2 MJ/kg (Joardder et al., 2012). While the bio-oil fraction, obtained via charring biomass in low oxygen environments and at slow temperature ramping rates, had a 50% experimental yield and 30% solid char yield, it is not entirely clear how “dry” the liquid extract was or its inherent chemical properties in the study by Joardder et al., but it had good comparison to diesel (HHV of 28.6 for date seed oil vs. 45.18 for diesel) (2012). Another study was using ground raw date pits to reinforce polymer composite tensile strengths (Abdulsada & Hashim, 2018). It is important to note that both findings used ground date pits. A short review details most of the potential products obtainable from date pit pyrolysis, including fermentable bio-oil with a theoretical yield of over 250 kg per ton of fruit and bio-diesel obtained from the fatty acid contents of bio-oil (Demirbas, 2017). The charred seed in particular is encouraged to be used as an activated carbon source, with uses ranging from water filter medium to green transesterification catalyst (Belhachemi et al., 2009; Merzougui et al., 2011; Hilal et al., 2012; Salman & Abid, 2013; Mahmoudi et al., 2014; Abu-Jrai et al., 2017). Studies have also been conducted to consider sustainable resourcing of materials through waste date biomass refinery, designed to process fuel and materials found in desert regions (Al-Farsi & Lee, 2008).

At a local level in the Sultanate of Oman and more recently, researchers have been developing a biodiesel pathway sourced from date pits. Jamil et al. have started by focussing on the extraction of fatty acid heavy bio-oil from date pits, using a Soxhlet extraction method to separate the oil from the date pits (2016). In a related study, the source date pits were then recycled to build a green catalyst to facilitate increased bio-diesel trans-esterification and production from date pit biomass (Abu-Jrai et al., 2017). The extracted bio-diesel was analysed for its combustion characteristics, with the results being comparable to rapeseed and soybean oils as an alternative for the Sultanate (Hellier et al., 2019). Though many of the results are very diesel fuel oriented, one thing is clear: date pit bio-diesel is inherently cleaner than fossil diesel with lower exhaust particulates, while retaining many similar values such as heating values (43.14 vs. 41.27 MJ/kg, reference vs. date pit bio-diesel), viscosity and cetane number. However to justify if date pits can be used as a reliable solid biomass fuel source, they have to be examined by some common biofuel characterisation methods such as ultimate and proximate analysis, and special methods to measure grindability; lignin content and pyrolytic product content to see what hydrocarbons the extracted bio-oils would produce.

On this note, the following methods are presented and their uses:

- Ultimate and proximate analysis are used in many studies to observe the carbon content and provide estimates for the energy content of potential solid bio-fuels. These values can then be compared to other biofuels in the expectation that a trend can be seen between different samples and studies.

- Lignocellulosic content analysis such as Acetyl Bromide Soluble Lignin assay can help determine sugar and phenolic content, thus giving a rough expectation as to the potential bioethanol and phenolic platform chemical yields. As well as understand where most of the carbon from the previous analyses are located and how they contribute to the energy contents.

- Pyrolysis-GC/MS can give further insight into the solid materials pyrolysis products as it vaporises the material into gaseous components via flash pyrolysis. Again, giving insight into the distribution of hydrocarbon components as well as potential products of biomass high temperature treatments.

- Point load or hydraulic press to study the grindability of date pits before and after can show the effects of processing them whole and the ease of grinding them to useful powder as a secondary step instead of the initial steps.

From the data presented, the need for a renewables extraction process plant would be an opportunity that should be captured. According to Abu-Jrai et al., one of the main challenges preventing commercialisation of date pits in the energy sector is requirement of an efficient waste management system, collecting the waste biomass from across Oman. While waiting for this aspect to improve, alternative extraction methods will be developed in preparation for the future.

2.4. Biomass Assessment and Analysis Methods

2.4.1. Elemental/Ultimate Analysis

Elemental or ultimate analysis is meant to be used to outline the elemental composition of solid fuels, especially potential biomass fuels. This is carried out with focus on carbon (C), nitrogen (N), hydrogen (H) and oxygen (O) although other elements such as sulphur (S) and chlorine (Cl) may also be taken into account. This method compares potential fuels to notable ones such as coal in regards to carbon content, potential calorific content and clean burning capabilities. For example, having a high H/C ratio indicates higher potential to produce water during combustion. While a high O/C ratio indicates abundance of polar functional groups, potentially reducing calorific content and heat of combustion. Examples of biomass compared to coal can be observed in Table 2.1**Error! Reference source not found.**

Nasser et al. provides ultimate analysis on date pits of 8 palm varieties and presents mean values in comparison to other parts of date palm, as well as comparison to other lignocellulosics (Nasser et al., 2016).

Detailed ultimate analysis can give elemental composition of biomass, providing information that can explain specific phenomena and expectations during processing. Multiple studies have presented data on the different varieties of date palm. This data can benefit the biorefinery process by indicating potential uses and materials obtainable from date pit biomass as well as providing a means to compare the date pits with current fuels, delivering a brief answer to whether or not date pits can replace fuel as a renewable energy source.

2.4.2. Proximate/Thermal Analysis

Proximate analysis involves the use of thermo-gravimetric and calorimetric analysis to observe changes to biomass feedstock over temperature ranges. Proximate analysis is used to determine the moisture, ash, fixed carbon, volatiles and calorific contents of biomass and fuel sources. As with ultimate analysis, proximate analysis allows the comparison of biomass and other solid fuels with regard to how much chemical energy and content they possess. Moisture and ash are interesting values as they reveal how much energy would be wasted in the drying process, and how much excess weight is contributed to transportation costs. Fixed carbon and volatiles contents contribute toward the calorific content and thus, as observed by several studies (Demirbaş, 1997; Sheng & Azevedo, 2005; Yin, 2011) can be used to estimate the calorific content of biomass and in some cases the lignin content of the biomass (Demirbaş, 2002; Demirbaş, 2003). Table 2.1 also presents studied values of biomass, including the biomass of interest, date palm seeds (i.e. Stones or pits) and comparing them to coal.

Gathered proximate analyses give an in-depth understanding of the overall thermal reactivity and composition of date pits. Furthermore, comparing of date pit data to other parts of the date palm justifies its preference as a potential fuel source. Nasser et al. also link and correlate lignocellulosic data with date pit data, revealing that date pits have physiochemical properties similar to that of hardwood materials while also having the size and relative shape of olive stones (2016). This also suggests that research done to valorise olive stones can in theory be applied to date pits, inclusive of size considerations for the raw biomass. This information correlates with studies by Sait et al. where TGA data is collected to understand the thermal behaviour and stability of date pits; useful for when they are to be thermally processed (2012). This can be linked to studies that focus on lignocellulosic material, indicating the varying degradation behaviours of cellulose, hemicellulose and lignin (Sanchez-Silva et al., 2012). Similar physiochemical data can be found in a study by Babiker et al., showing that the different varieties have little difference in volatile matter, fixed carbon and ash content, key indicators in the viability of biomass as fuel (2013). Collectively, this information gives better insight into preparing methods for refining a readily available source of waste biomass, maximising the value of date pits using biorefinery processes.

Table 2.1 Proximate and ultimate analysis of referenced biomass including date palm biomass.

Type	**Proximate Analysis (wt%)**[1]			**Ultimate Analysis (wt%)**[1]				**References**
	VM	**FC**	**Ash**	**C**	**H**	**N**	**O**[2]	
Bituminous Coal	23.53	62.54	13.93	66.5	4.4	1.2	13.3	(Coppola et al., 2015)
Brewers Spent	79.22	16.46	4.32	53.50	7.27	4.89	34.04	(Olszewski et al.,

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[1] Analyses are in terms of dry biomass weight % basis

[2] Calculated by difference

Grain				1	3	3	3	2019)
Coconut Shell	77.19	22.1	0.71	50.22	5.70	0.00	43.37	(Channiwala & Parikh, 2002)
Sugarcane Bagasse	83.66	13.15	3.20	45.48	5.96	0.15	45.21	(Channiwala & Parikh, 2002)
Date Pit (Date Palm Stone)	83.33	14.94	1.4	47.14	6.63	0.9	45.33	(Nasser et al., 2016)
Date Palm Trunk	78.53	17.61	3.86	44.46	5.75	0.55	49.24	(Nasser et al., 2016)
Olive Stone	78.30	19.50	2.20	49.00	6.10	0.80	42.00	(Cordero et al., 2001)
Pecan nut Shell	61.7	24.9	3.6	51.1	5.4	0.7	43.5	(Aldana et al., 2015)

2.4.3. Lignocellulosic Composition and Analysis

As this study will focus on biomass processing, it is important to obtain information on the lignocellulosic fractions with particular interest in the lignin content. It is known that most terrestrial plants contain some of the most abundant biopolymers in the world; cellulose, hemicellulose and lignin. While this study aims to extract as much energy efficient material from date pits as possible, there is also an opportunity to justify the analysis and focus on the lignin fraction of date pits, and the subsequent extraction and separation therefrom as they can provide high value and high energy fuel additives and platform chemicals for various industries.

Cellulose is acknowledged as one of the most abundant natural polymers (Brigham, 2017), and provides structure and water retention for plants. It is comprised of repeating glucose units, linked by oxygen attached in a glycosidic bond as can be seen in Figure 2.3**Error! Reference source not found.**. This then leads to constituting the plant cell walls as the chains become linked through hemicellulose-lignin links or hydrogen bonding between them. Analysis of cellulose content is beneficial to the research in that cellulose can and has been used to produce glucose as a fermentation feedstock (Shafizadeh et al., 1979; Sasaki et al., 2000; Huang & Fu, 2013) or gels and composites (Liu et al., 2017), and thus would prove as useful by-product if not at least viable animal feed. A key note to observe throughout the revised studies is that the cellulose (and subsequently the lignin and hemicellulose contents) content is generally reported on an extractives-free basis. Extractives include substances that would normally dissolve with little effort (such as simple sugars) in water. This fraction can vary as do the other fractions between biomass samples and sources as observed in a study by Nasser et al.

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[1] Dry ash-free basis

(2016), where the extractives is listed as well as the respective fractions. Thus the lignocellulosic content is inherently reported as a "fraction of a fraction" and can seem skewed. It is noteworthy that an "extractives-free" ground date pit sample is unlikely to have the same composition as an "extractives-free" whole date pit, as the "extractives" are unlikely to be easily removed from the whole date pit due to the hard shell.

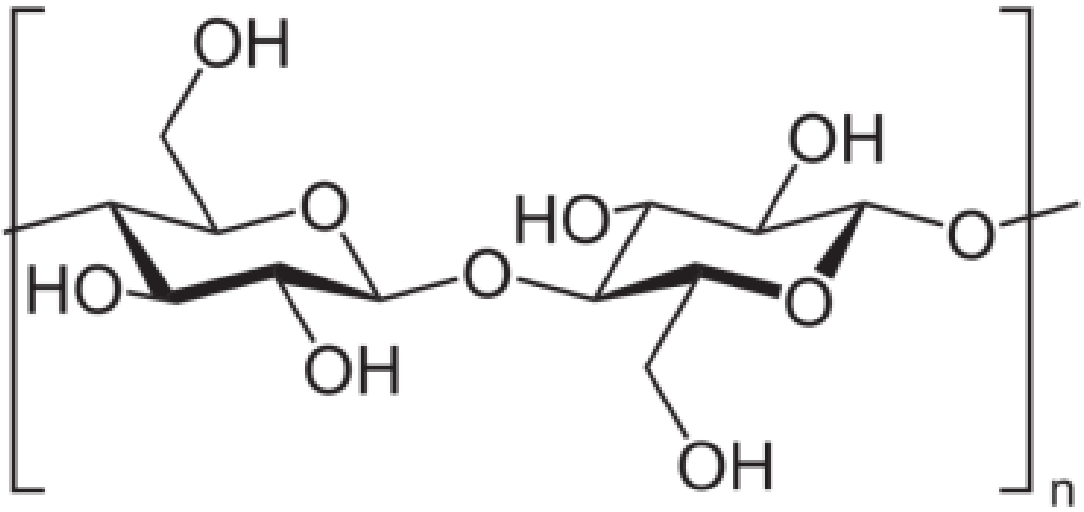

Figure 2.3 A part of the cellulose polymer chain. The glycosidic bond is seen linking the glucose units. (Nishiyama et al., 2002)

That being said, the quantitative analysis of cellulose has been approached from chemical and thermal methodologies. The Van Soest method is a highly cited method, and is considered to be rapid and effective in determining cellulose content within the cell wall (Van Soest & Wine, 1967; Liu et al., 2017). Although useful, this method requires the user to be knowledgeable in chemistry or facilities that have safe access to the essential solvents. This issue is more prominent in the acetyl bromide lignin quantification methodology for the specific reason that the use of highly toxic acetyl bromide can only occur in certified labs. Alternatives do exist however, but at the cost of accuracy such as the estimation of lignocellulose quantities by deconvolution of TGA peaks (Pang et al., 2014; Rego et al., 2019). While this methodology is relatively inaccurate, considering the availability and relative ease of use, it may be considered for larger scale operations due to the diverse nature of biomass where accuracy in one sample is hollow in the face of the next sample.

The issue of inaccuracy is further examined and observed in the analysis of lignin quantities present in biomass. As Hatfield and Fukushima have reviewed multiple, different chemical based methods for quantifying lignin in biomass, they conclude that there is no all-round accurate method but rather that consistency in evaluation is a more vital factor (2005). On the subject of chemical based methods, the acetyl bromide soluble lignin (ABSL) Assay is regarded as one of the more accurate methods and is widely used to determine pre-processing lignin content (Fukushima & Hatfield, 2001; Barnes & Anderson, 2017). Other chemical based alternatives include Klason method and the use of thioglycolic acid, but upon comparison these methods have shown to be less effective than the ABSL method. (Moreira-Vilar et al., 2014). While these chemical methods are lauded as accurate, the use of acetyl bromide has safety issues and requirements that would not be readily available in many engineering labs. And thus alternative methods should be considered, especially for the bioenergy and thermal processing fields.

An alternative that will be considered and used prominently throughout this study is the use of thermo-gravimetric analysis, to obtain proximate analysis as well as gross calorific value (GCV) and lignin content estimations. Demirbaş has extensively studied the use of TGA in these aspects, and the produced equations should be considered for use (1997; 2001; 2002; 2003). This methodology provides multiple relevant data points from one set of experiments. In using TGA, the data can also be used to observe critical thermal stages where major components degrade significantly before others. This information can then be utilised to design processing methods with the objective of maintaining the cellulose and lignin fractions. Though the TGA method provides estimations, it concurs with the conclusion that accuracy is not attainable while providing extra relevant information for the remainder of this study. Using this method can allow determination of the effectiveness of pre-treatment and processing methods, in a consistent and comparative manner.

There is an issue of contradiction between several TGA studies, most noteworthy between Singh et al. (2009) and Yang et al. (2007), where the former infers that lignin has 2 degradation peaks while the latter states that the region the lignin degradation peak forms is designated for hemicellulose. This will lead to a potential misinterpretation of the results, especially due to the heterogeneous natures of both hemicellulose and lignin which could possibly have branches that degrade at lower temperatures. However it is strategic to note as stated above, lignin is a primary source of fixed carbon content and thus it can be concluded that the majority of lignin degrades at higher pyrolysis temperatures in comparison to cellulose and hemicellulose found in the same biomass samples.

2.4.4. Pyrolysis – Gas Chromatography/Mass Spectrometry (Py-GC/MS)

Py-GC/MS is an experimental method that essentially attaches a pyrolyser or pyro-probe, capable of flash pyrolysis and vaporising solid material, to a GC/MS. It has seen early uses in biomass study such as understanding the degradation of cutins (water proof polymerised esters found in plant cuticles) in plant fossil extracts (Nip et al., 1986). For this research, it will be investigated as a potential method for characterisation of the raw date pits and extractables, and possible lignocellulosic quantification or estimation. Using Py-GC/MS to analyse the pyrolysates, the possibilities will be outlined in this section.

Of the applications of Py-GC/MS, the information available is useful for building an analysis methodology for date pits and the processed outcomes. Py-GC/MS is presented by Biller and Ross as a novel method for microalgae nutritional content analysis, while also comparing the results to traditional analytical methods for protein, carbohydrates and lipids (2014). Their method requires the selection of compounds to quantify the respective lipid, protein and carbohydrate peaks. Though this is useful for studying the nutritional content, other studies pursue more thermally based characterisations and goals and would be more applicable with this thesis. An example of this can be seen in work by Hidayat et al., where they conduct bio-oil examination post production from cogongrass (2018). In conjunction with thermal analysis, the pyrolysis products are also observed, revealing the yield of aromatic/phenolic compounds obtained from biomass (See Table 2.2). Though this study was mainly focused on identifying lignin based phenolics, the pyrolysis products of cellulose and hemicellulose can be seen in significant and detectable quantities primarily as furans. It is evident in their research that it is possible to quantify and estimate lignocellulosics without the need for a standard, instead relatively to the overall mass of the sample. Perhaps this can be assisted with mass loss and lignin estimation information obtained from proximate analysis.

Table 2.2 Components identified (in order of peak resolution) in the py-GC/MS of *Imperata cylindrica* at temperature 500 °C (Hidayat et al., 2018).

Component	**Formula**	**MW**	**Peak Area (%)**	**Classification according to author**
Cyclopentadiene	C_5H_6	66	1.60	Cycloalkenes
3-Methylfuran	C_5H_6O	82	1.33	Furans
2,5-Dimethyfuran	C_6H_8O	96	0.52	Furans
Acetic Acid	$C_2H_4O_2$	60	4.10	Organic Acid
Toluene	C_7H_8	92	1.68	Aromatics

Ethylbenzene	C_8H_{10}	106	0.72	Aromatics
p-Xylene	C_8H_{10}	106	0.32	Aromatics
1-Hydroxy-2-butanone	$C_4H_8O_2$	88	1.66	Ketones
Styrene	C_8H_8	104	0.50	Aromatics
Furfural	$C_5H_4O_2$	96	3.72	Furans
Propylbenzene	C_9H_{12}	120	0.58	Aromatics
2-Methyl-2-cyclopenten-1-one	C_6H_8O	96	0.65	Cycloalkenes
2-Furanmethanol	$C_5H_6O_2$	98	1.18	Furans
2-Hydroxy-2-cyclopenten-1-one	$C_5H_6O_2$	98	0.53	Cycloalkenes
5-Methylfurfural	$C_6H_6O_2$	110	0.65	Furans
2,3-Pentanedione	$C_5H_8O_2$	100	0.26	Ketones
3-Methyl-2-cyclopenten-1-one	C_6H_8O	96	0.47	Cycloalkenes
Benzeneacetaldehyde	C_8H_8O	120	ND	Aromatics
2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	110	0.68	Cycloalkenes
2-Hydroxy-3-methyl-2-cyclopenten-1-one	$C_6H_8O_2$	112	1.58	Cycloalkenes
Guaiacol	$C_7H_8O_2$	124	11.56	G-Lignin
2-Methylphenol	C_7H_8O	108	1.97	H-Lignin
p-Cresol	C_7H_8O	108	3.00	H-Lignin
2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	138	3.00	G-Lignin
2,4-Dimethylphenol	$C_8H_{10}O$	122	1.01	H-Lignin
4-Ethylphenol	$C_8H_{10}O$	122	3.92	H-Lignin
4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	152	4.20	G-Lignin
Indanone	C_9H_8O	132	2.56	Aromatics
4-Vinylguaiacol	$C_9H_{12}O_2$	150	17.82	G-Lignin
2,3-Dihydrobenzofuran	C_8H_8O	120	11.17	Furans
2,6-Dimethoxyphenol	$C_8H_{10}O_3$	154	2.66	S-Lignin
2-Methoxy-4-propenylphenol	$C_{10}H_{12}O_2$	164	1.62	G-Lignin
Hexadecane	$C_{16}H_{34}$	226	0.76	Misc.
Propenylguaiacol	$C_{10}H_{12}O_2$	164	3.61	G-Lignin
1,2,4-Trimethoxybenzene	$C_9H_{12}O_2$	168	0.76	S-Lignin
Isovanillin	$C_8H_8O_3$	152	1.13	G-Lignin
5-tert-Butylpyrogallol	$C_{10}H_{14}O_3$	182	0.63	Misc.
1-(3,4-Dimethoxyphenyl)ethanone	$C_{10}H_{12}O_3$	180	0.80	Ketones
Guaiacylacetone	$C_{10}H_{12}O_3$	180	0.76	G-Lignin
(2E)-3,7,11,15-Tetramethyl-2-hexadecen-1-ol	$C_{20}H_{40}$	280	2.85	Misc.
2,6-Dimethoxy-4-allylphenol	$C_{11}H_{14}O_3$	194	0.80	S-Lignin
Methyl hexadecanoate	$C_{17}H_{34}O_2$	270	0.21	Ester
n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256	0.48	Organic Acid

The methodology and results used in the aforementioned material are reflected in a study tracing the origins of compounds found in bio-oils, albeit using slightly different pyrolysis conditions and the authors categorising the resulting pyrolysates differently (Subagyono et al., 2016). Though research by Gao et al. adheres to pyrolysing biomass at 600 °C, obtaining results that show the general products of pyrolysis under these conditions and stating that acetic acid is the main pyrolysis product of hemicellulose, so by using this information the researcher can infer that cellulose and lignin degradation contribute minimally to acetic acid formation (2013). This is proven for lignin when del Rio et al. analyse lignin samples using Py-GC/MS, recording almost no peaks lighter than phenol, given they were examining the pyrolysates of lignin-rich biomass and provided no temperature information of conditions used for pyrolysis (2007). In another study on lignin pyrolysis, it is stated that cellulose cannot be easily estimated, as the charring and degradation of cellulose pyrolysates may not be captured in the chromatograms (del Río et al., 2005). This study by del Río et al. also focuses on lignin pyrolysis to compare and understand the ease of delignification between biomass samples based on lignin and hypothetical cellulose contents (2005). Another study relevant to this thesis involves analysis of water insoluble lignin, showing an overlap of known pyrolysates such as guaiacol and p-cresol (Scholze & Meier, 2001). Attributing the presence of guaiacols and sinapyl alcohols, being key products of lignin monomer pyrolysis respectively, may facilitate more accurate estimation of lignin content by Py-GC/MS. The relative stability of phenolics would also add to quantification accuracy as phenolic content would be directly proportional to lignin content (one benzene ring per lignin monomer in the chain). The accuracy of Py-GC/MS is inherently tied to the pyrolyser temperature and flash exposure time (Lu et al., 2011). By varying the flash pyrolysis temperature and time, previous research gives an idea of the degradation mechanics during processing. The work of Lu et al. centres on the formation and degradation of cellulose products, observing a general increase in yields of levoglucosan and furans up to 600 °C. This will further help refine the project methodology as it can insure that most of the cellulose has pyrolysed without degrading the lignin polymer chains more than necessary, painting an accurate picture of lignocellulosic content.

This combined knowledge will help understand and design an analysis methodology for Py-GC/MS. Based on the presented literature, this thesis can briefly benefit from the use of Py-GC/MS when analysing solid samples. Analysis of the raw date pit material, extracted fibres and dried bio-oils in a simultaneously quantitative and qualitative manner can provide information in niche sectors of biomass and Arabian Gulf renewables, and benefit this research study to determine initial quantities, potential yields and purities of extracts. Py-GC/MS still leaves much room for improvement on the subject of cellulose, but may prove adequately useful within the lignin based scope of this research for phenolic characterisation and yield.

2.4.5. Density, Hardness and Grindability

Due to the shape of date pits, there may be inherent difficulties when measuring some of the mechanical properties of the raw biomass. Knowledge of this information would be beneficial regardless for this research, since it may provide another piece of comparable data when analysing raw and processed date pits. Grindability of date pits and lowered density (which can be roughly correlated to hardness)[1] could be indicators post treatment for ease of consumption as animal feed or biorefinery feedstock. Literature will show how the density and grindability are key features that may be considered for this thesis.

As a general reference, studies have found that date pits have bulk densities between 450 – 730 kg/m^3 (Babiker et al., 2013; Abu-Jdayil et al., 2019), depending on the variety. For reference, a table of bulk densities comparing date pits with known hardwoods is presented in Table 2.3. It is evident that date pits have similarity in bulk density with hardwoods, expanding options for mechanical processing by using apparatus such as wood chippers since the hardness of date pits can be compared to that of hardwoods. The relatively small size of date pits as well as their low bulk would make this difficult, as these machines are meant to make large piles of wood into workable biomass pellets.

Table 2.3 Bulk densities of known materials and researched date pits.

Material/Biomass	**Bulk Density (kg/m^3)**	**References**
Date Pit (Safawi)	550	(Babiker et al., 2013)
Date Pit	534	(Abu-Jdayil et al., 2019)
British Birch	670	(Heirloom Kayak, 2012)
English Brown Oak	740	(Heirloom Kayak, 2012)
Poplar	350 - 500	(Heirloom Kayak, 2012)
Hickory	830	(Heirloom Kayak, 2012)
Sycamore	400 - 600	(Heirloom Kayak, 2012)

A ball mill or a Wiley mill may be more suitable for crushing date pits into a fine powder; however this may end up mechanically breaking down the lignin polymer chains (Bai et al., 2013). Milling provides the chance to obtain the date pit powder while lowering the intrinsic value of the lignin fraction from processing the powder. A study aimed at investigating the structural changes that occur in milled wood lignin under various conditions found that increasing milling time provided a higher lignin

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[1] Though hardness and density are roughly correlated, this is mainly true for minerals and is entirely dependent on the molecular makeup of the material and packing structure. (Railsback, 2006).

yield, but the disruption to the overall wood structure caused by breaking down carbohydrate linkages (dubbed phenolic ,β-O-4) between the lignin monomers led to smaller lignin chains (Ikeda et al., 2002). A vital aim of this thesis would be to get lignin with as little degradation as possible, as the economic benefit is attached to its purity which is dependent on the processes and molecular size (Ľudmila et al., 2015). Therefore it is encouraged to propose a method that would separate the valuable lignocellulosic material from the biomass while softening the date pits for later consumption as soft pellets.

As for grindability, while there is little to no information regarding the relationship between density and grindability of biomass, hypotheses can be drawn that they are proportional to each other such that as density increases, grindability decreases due to close packing/bonding of the internal structure. This can be seen in a torrefaction study, where the process plays a role in reducing the energy required to grind biomass by up to 90% of the energy required to mill untreated biomass (Wang et al., 2017).This can be attributed to the decomposition of large lignocellulosic components such as hemicellulose and cellulose chains and linkages, weakening the overall bulk biomass structure and integrity. Based on results by Phanphanich and Mani, it is also observed that there is an obvious change in bulk density contrary to their expectations (Pine chips: 381 kg/m^3 decreasing to 331.8 kg/m^3 and increasing to 400.2 kg/m^3, when torriefied at 250 °C and 300 °C respectively) (2011). This data reinforces the hypothesis that the density and grindability are connected up to 250 °C. The increase in grindability as the density decreases may be caused by reducing the number of voids in the sample, thereby “decreasing” its density while maintaining the shape and volume of the sample.

This work will therefore make use of thermal processing methods to soften date pits, to improve the value of biomass, extract high energy or valuable materials and to make it easier to transport and mechanically process for other industries. Since the grindability and bulk density are somewhat related and tied to the processing temperature of the biomass, a method should be designed to at least pre-treat date pits and make them mechanically processable, in the outcome that no viable materials are separated from the date pits.

2.5. Biomass Processing Methods and Technologies

With regards to the processing of a potential biorefinery feedstock, several conventional methods will be looked at and considered for this purpose. These methods will be reviewed on the basis of primary obtainable products, processing parameters and mechanisms at play within the biomass and how these can be managed. Understanding the interactions that occur between the biomass and process environment can provide insight into the method design, providing a basis of information to justify a suitable way to valorise waste date pits into the desired products for this thesis.

Mechanical methods such as milling and ultrasonic treatment will not be considered for this study because they would produce pellets or at least small processable material from large biomass feedstocks, while date pits already come in pellet sizes or already industrially provided in powdered form as a flour alternative for some households, using date pits obtained from the fruit used to produce date cakes etc. (Al Barakah Dates Factory, 2017). Some of the remaining commonly used and studied methodologies fall under chemical treatments, which included in this review but are not limited to:

- Ionic Liquids (IL) Extraction
- Acid Hydrolysis
- Organosolv Extraction
- (Dry) Pyrolysis
- Liquid Hot Water (LHW)/Hydrothermal Pyrolysis

2.5.1. Ionic Liquids Extraction

Beginning with one of the more chemically composite methods, ionic liquids can be custom made to purpose since the 1930s and used to dissolve specific components within biomass. A study by da Costa Lopes et al. goes into detail about the use of 1-ethyl-3-methylimidazolium acetate as a means to dissolve lignocellulosic components from wheat straw biomass (2016). In their study, the IL dissolved all lignocellulosic fractions and was later treated with different substances and resins, extracting the specific fractions in post treatment of the wheat straw biomass. This method seems highly reliable in a multistep separation of biomass components within a biorefinery, as the results show high recovery of cellulose and the IL but not as much for lignin. Another study followed an economic approach, developing low cost ILs for similar purposes (George et al., 2014). The IL was used to selectively extract glucose from biomass, resulting in relatively high hydrolysis yields for this study (75% efficiency when compared to a standard IL). In a similar fashion, Gschwend et al. looked into the cost efficient extraction of lignin (2016). The results show that a majority of lignin and hemicellulose dissolved in the IL, hydrolysing the hemicellulose and making it unrecoverable while leaving behind a cellulose rich pulp, while the lignin is dissolved in solution and can be extracted later. This can simplify upcoming processing steps by presenting a solid glucose based fraction, and a liquid phenolic fraction which can incorporate lignin precipitation methods. Post processing of the phenolic fraction has also been considered, where a study focused on lignin depolymerisation and conversion into simpler phenolics using IL (Nanayakkara et al., 2014). The authors present the possibility of using neutral ILs in more than one biorefinery process, or at least in a step other than pre-treatment of biomass. The main issue with ILs is that although they are recyclable, they are still inherently toxic to the environment.

2.5.2. Acid Hydrolysis

The paper industry has already been using this method for a long time to remove lignin from cellulose rich wood and producing paper. Acid hydrolysis has been one of the more popular industrial methods of biomass treatment. The sulphite process was primarily used to process wood biomass, extracting a lignin free and cellulose rich pulp to be consequently made into paper. This method involves the use of sulphur based acids and alkaline metal solutions, with various alternatives being studied with consideration toward finding cost effective or environmentally nonthreatening methods.

One such study uses pre-sulfonated activated carbon to hydrolyse cellobiose (short chain cellulose) into glucose, with good reusability and good conversion rates (Foo et al., 2015). This study presents a potential environmentally friendly method to produce fermentable sugars, as well as possibly use carbonised biomass. Another paper suggests the combined use of previously mentioned ionic liquids with acid hydrolysis, significantly lowering the hydrolysis of biomass into fermentable sugars (Binder & Raines, 2010). This study provides several economic benefits such as avoiding enzyme usage (which is common to breakdown the sugars and weaken the lignocellulosic structure but can take several days to complete), and significant time and temperature reduction in comparison to enzymatic hydrolysis which can take days with delicate catalysts/enzymes. Weaker acids have also been studied as alternatives to observe the effect of hemicellulosic decomposition on potato peels (Lenihan et al., 2010). This study showed promising results, with high sugar yields (55g/100g of potato peel) under relatively less demanding conditions. Alternatively, a study conducted the hydrolysis of biomass using an alkaline pre-treatment prior to acid hydrolysis (Kassaye et al., 2017). The outcomes have shown that alkaline pre-treatment before normal acid hydrolysis had significant results, allowing reduced usage of acid solution for greater effect, providing easier hydrolysis conditions for greater sugar yields. The main objective of these research papers is to provide a feedstock for bio-ethanol production, providing another obtainable product for this thesis.

Evidently and due to its rampant use in the paper making industry, acid hydrolysis would see its use in the biomass industry to produce fermentable cellulose based sugars, which in turn produce bioethanol as a fuel, and has been known to yield Kraft lignins, which are lignins obtained from acid/alkaline hydrolysis pre-treatments and account for 85% of lignin produced worldwide. It should also be noted that despite the beneficial yields, the method has been scrutinised for being unsafe to the environment as waste is sent into streams and sea pipelines. Thus, there is an apparent need to seek substitute methods as well as feedstocks and products. Although this methodology is useful, the environmental aspects encourage consideration of other potential methods, yet it will be considered as a potential substitute to this thesis.

2.5.3. Organosolv Extraction

Lignin is naturally hydrophobic and does not dissolve easily in aqueous environments (Gould et al., 2016). Organosolv is another method used primarily in the papermaking industry, deriving from the use of organic solvents to pulp biomass and dissolve lignin and hemicellulose. It was made as an environmentally nonthreatening method compared to previous pulping techniques. Another benefit to this is the capability to precipitate and collect lignin as added value to the solubised waste stream, providing high quality and long chained lignin powder. Organosolv lignin also has the added benefit of maintaining its hydrophobic nature, giving rise to more uses than sulphite or Kraft lignin (Gordobil et al., 2017). Despite its relative efficiency and environmental benefit in large-scale papermaking, research is still being conducted to observe the differences in solvent use and optimisation of waste stream extracts by reducing sulfonated lignin production, which produces water-soluble lignins at the cost of using toxic sulphuric acid.

One study revealed the diversity of organosolv solvents as well as their miscibility, with Lu et al. looking into increasing lignin extraction efficiency (2012). By treating biomass with the organic solvent mixtures, they were able to observe that 1-4 butanediol had great delignification efficiency, producing high yields comparable to acetic acid-water. The 1-4 butanediol had a slight antioxidant inhibiting effect on the biomass, thereby preserving more of the pulp. Acetic acid functions by degrading carbohydrates and thereby liberating lignin from the surrounding material. Another mixture that was studied and appears commonly in other research is ethanol-water pre-treatment, a mixture that encouraged the breakdown of lignocellulosics by dissolving lignin and celluloses and should not be overlooked in low temperature organosolv pre-treatments. This is reflected in studies by Zhao et al. (2009) and Geng et al. (2012), among other research articles. Zhao et al. thoroughly outlines the organosolv pre-treatment process, with the expectation of using this method to prepare the biomass samples for enzymatic hydrolysis (2009). Observing that ethanol organosolv inhibits lignin recalcitrance and precipitation prior to separation from biomass pulp. This is also seen Geng et al. where they used H_2O_2 as a post-treatment step to ensure higher lignin yield and better ethanol fermentation yields (2012).

2.5.4. Pyrolysis

Pyrolysis of biomass is simply thermal degradation without the presence of air/oxygen. Due to lacking oxygen, wood would inherently carbonise and give rise to charcoal. However, there is also the evolution of volatile compounds, H_2O and CO_2 that is formed from internal devolatilisation and breakdown of bio-polymers. Research has taken steps into understanding the formation of the bio-oils and optimising their capture from various biomass sources, aiming to improve the value of waste biomass into useful and valuable bio-gas and bio-oil sources.

Hemicellulose would be the first bio-polymer to breakdown in pyrolysis. A review by Zhou et al. has in depth analysis of sugars that comprise the hemicellulose macrostructure, pointing out that the majority sugars are xylans or xylose monomer chains (2017). Depending on the structure and purity of xylose, which can closely resemble glucose (and subsequently starch and cellulose), the decomposition occurs in conventional temperatures higher than 190 °C and generally overlaps with the cellulose pyrolysis range. The yields can include a wide range of products with the bulk being light volatiles that introduce acidic conditions within the biomass, such as acetic acid, furfural and CO_2. This is corroborated by Hidayat et al. where they found that cellulose and hemicellulose produced furans during pyrolysis, formed as a result of a dehydration reaction due to the heat breaking weaker intermolecular bonds (2018). Coupled with the knowledge of degradation temperatures and pyrolytic behaviour, this information can help build better approaches to utilise the hemicellulose fraction in pyrolysis methods and increase its value in the date pit biomass.

The pyrolysis of cellulose follows the degradation of hemicellulose due to sharing pyrolysis ranges and similarities in structure. However the lack of 4C1O rings makes cellulose overall stronger and encourages the formation of pyrans and acetic acid, as well as other glucose-based pyrolysis products such as levoglucosan, which is a highly sought after cellulose pyrolysate. This is shown in Py-GC/MS analysis, revealing levoglucosan and CO as by-products of pure cellulose pyrolysis (Lin et al., 2009). Also when testing different temperature conditions for fast pyrolysis, it was found that larger molecules like levoglucosan had greater yields at higher temperatures (600°C+) (Lu et al., 2011). And since levoglucosan is reportedly thermally stable, it would most likely linger if not given a chance to evaporate and accumulate within the biomass during the pyrolysis. A more in depth analysis of levoglucosan formation has been outlined by Zhang et al. and should be referred to understand which pathway may occur in different pyrolytic settings (2013). It should be noted that contradictory studies showing the formation of levoglucosan at slower pyrolysis speeds were published, however the “slow” ramp rates were 1 °C/s for a small sample which can be seen as relatively fast when approaching 450 °C (Yu et al., 2019). Assuming most of these by-products are broken down further into acetic acid and water during flash pyrolysis, it is encouraging to see that the formation of pyranoses and oligosaccharides can be attributed to cellulose pyrolysis than to the degradation of hemicellulose.

The pyrolytic analysis of lignin is notably more difficult since lignin is essentially very stable, both chemically and thermally. It is thus more likely to form tar-like products that turn into char or vaporise as large molecules at high temperatures in the pyrolysis vessel. In the event that pyrolysis does occur in the lignin polymer, Kawamoto has detailed several possible reactions that may occur (2017). With the majority of reactions occurring above 400 °C, the yields are usually liberated phenolics, catechols and creosols as the energy acts on the bonds between the lignin monomers and connected hemicellulose side chains. There is also a small chance for phenolic radical species to degrade into light volatiles. This is backed up by data provided by Asmadi et al. where they observe the secondary pyrolysis reactions of catechol, and the breakdown of the lignin monomers into the previously mentioned phenolic products and eventually coke, tar and gas (Asmadi et al., 2011; 2011; 2012). These studies collectively show that at certain temperatures, lignin has three possible pyrolytic pathways: 1) carbonise as fixed carbon; 2) dissolve as phenolics in bio-oil extracts or 3) breakdown into gaseous volatiles that would be difficult to capture. Until then, lignin can be assumed to generally be unaffected outside of losing its linkage to hemicellulose and cellulose.

When looking at the random overall composition of lignocellulosic biomass, the anatomy of useful products can be generated through pyrolysis and methodologies to obtain said products. Pyrolysis is heavily energy dependent and rate dependent. It would be an interesting method to implement in this study in the hopes that it can liberate the lignin fraction while generating a bio-oil value stream.

2.5.5. Liquid Hot Water/Hydrothermal Pyrolysis

Liquid Hot Water (LHW), otherwise known as subcritical water or hydrothermal treatment, generates a unique environment that can be beneficial in biomass pre-treatment. By controlling increased pressures and high temperatures, LHW can become a uniquely non-polar solution, where the water molecules have a high chance of breaking into radicals and using radical chemistry and breaking biopolymers into base fragments (Jiang et al., 2020; Zheng et al., 2020). This solution increases the potential breakdown of lignocellulosic material such as hemicellulose at its degradation points (between 150 – 250 °C). Capturing volatiles in the vessel and solution, as well as several other applications have been studied and could determine how to proceed with processing date pit biomass.

LHW treatment is effectively low temperature pyrolysis, with the added benefits of chemical hydrolysis, weak acidolysis and non-polar solubility, thus affecting the organic molecules in that manner. This can be seen in research by Katritzky et al. where they study a variety of potential chemical reactions that occur in hot water under pressure, revealing pathways that lead to stable pyridine formation or breakdown of phenolic chains in these conditions (1996). This eventually relates to the processing of biomass in LHW conditions, since they consist of cyclic organic bio-polymers (phenolic lignins and sugary cellulose/hemicellulose). The bio-polymers that make up lignocellulosic waste biomass have been studied to observe their reactivity in hydrothermal environments, with differing goals including extraction and conversion of large chains into easily marketable resources. For example, the decomposition of cellulose in 320 °C slurry has been seen breaking down polymer chains and release glucose monomers (Sasaki et al., 2000). Similarly, a study has focused on the production of bio-ethanol from the extracted fractions (liquid and solid sugar yields) generated from LHW pre-treatment (Zhuang et al., 2016). Another study had previously added water to an acidic ionic liquid, combining two methods and was able to obtain high yields of monosaccharides for fermentation into bio-ethanol (Binder & Raines, 2010). Analysis of the pathways hemicellulose and lignin taken during hydrolysis and decomposition, showing the breakdown of hemicellulose into useful materials such as furfural, conservation of cellulose and glucose and migration of lignin out of cell walls into a collectable product were conducted in several studies (Ibbett et al., 2011; Yu et al., 2013; Zhuang et al., 2016). These studies collectively justify that LHW is viable as an environmentally friendly biomass processing technique.

The chemical aspect comes from the duality of subcritical water pH (both acidic and basic as the water molecules split into H^+ and OH^- ions and radicals) and the loss in polarity, adding to the reactivity and solubility of LHW with organic, non-polar biomass material. LHW is also shown to increase in acidity over the course of the process, due to the formation of acidic compounds and making the ideal environment to process lignin (which is usually extracted using H_2SO_4). This can be seen in the treatment of apricot shells, where acetic acid, formed from hemicellulose degradation, increased chances of deacetylation of xylans (Corbett et al., 2015). This shows potential selectivity for xylan removal and lignin liberation, while keeping cellulose protected. Combining this research reveals the usefulness of LHW as a pyrolysis medium as it can simultaneously treat biomass and capture the extractives.

Overall, LHW shows significant potential as a suitable and effective method for softening biomass for value added treatment and modification into a microwave method. Based on some of the application outlined above, LHW can be used to process date pit biomass by significantly softening them in breaking the internal structure apart, preparing them for further treatment and refining. Meanwhile, the resulting solution of water soluble volatiles and captured extractables can be utilised directly for fermentation and bio-ethanol production, assuming they are mainly sugar based derivatives. The conditions and renewability of LHW provides a beneficial avenue to process biomass and test in microwave conditions.

2.6. Microwave Theory

Microwave ovens have been utilised as a method to heat food and materials, to cook food in seconds by harnessing energy in the microwave frequency range (300 MHz to 300GHz) of the electromagnetic spectrum. Most industries that implement microwave commonly use 915 MHz and 2450 MHz frequencies for a variety of purposes. Microwaves are generated from a magnetron, an oscillator where a magnetic field interacts with electrons and produces a resonant microwave frequency, dependant on the oscillator’s dimensions. This in turn produces an electric field that can induce movement of polarisable and charged particles within a medium, causing the material to heat as energy is dissipated due to the resistance to this motion via friction and other intermolecular forces. Due to their interactions, microwaves are known to heat volumetrically, as opposed to conventional ovens that rely on convection heating, thereby reducing processing time significantly.

2.6.1. Dielectric Properties

The extent to which a material will interact with microwaves at a given frequency can be quantified by the dielectric properties. The dielectric constant or relative permittivity, expressed as ε_r, is a frequency dependant value that denotes the capability of a material to interact with an electric field as well as a relative measure of its polarity (see Equation 2.1) (Meredith, 1998). The dielectric constant is known to decrease in solvents as they get hotter, with the ε' of water starting from 80.1 at 20 ˚C and dropping to 34.5 at 200 ˚C, measured at a frequency of 2.45 GHz. Dielectric loss, mathematically denoted as the imaginary part of the relative permittivity equation ε" (where j is the imaginary part), is a material's capability to dissipate electromagnetic energy and convert it into heat. This is usually expressed in the equation for the loss tangent or tan δ (see Equation 2.2), such that a lossy material is highly efficient in dispersing microwave energy as heat, usually with a loss tangent ≥0.1. Other notable trends include a relation of a liquid solvent polarity to its dielectric constant, which can in turn affect its loss factor. More polar solvents have higher loss tangents, and higher loss tangents leads to a better conversion to heat. These properties are essential in understanding the heating mechanics of microwaves, so that better methods may be developed to optimally apply microwave energy in a biorefinery setting.

$$\boldsymbol{\varepsilon_r = \varepsilon' - j\varepsilon''}$$

Equation 2.1

$$\boldsymbol{\tan\delta = \frac{\varepsilon''}{\varepsilon'}}$$

Equation 2.2

Several substances and their dielectric properties can be found in Table 2.4, some of the changes in water can be seen in this table. It should be noted that the loss tangent is a reflection of the dielectric loss, in that the higher the loss tangent, the higher the dielectric loss and the more likely the input microwave energy will be translated into heat losses.

Table 2.4 Some examples of substances and their dielectric properties at 2.45 GHz. (Editor, 2021)

Material	Dielectric Constant	Loss Tangent
Water (20 °C)	80.4	0.157
Water (100 °C)	55.3	-
Water (200 °C)	34.5	-
Alumina	9.0	0.0006
Borosilicate Glass	4.3	0.0047
Concrete (Dry)	4.5	0.0111
Corn Oil	2.6	0.0077
Paper	3 – 4	0.0125 – 0.0333
Wood	1.2 – 5	0.0040 – 0.4167

2.6.2. Microwave Interactions

Based on what is known about microwaves and how they generally interact with pure substances and materials, there is a need to understand the behaviour of matrices such as lignocellulosic biomass when exposed to an electric field. Of the aspects that heavily impact biomass during microwave radiation, the concepts of selective heating and microwave interactions with different substances within biological media will be discussed. These concepts will help formulate optimised methods of processing biomass using microwaves, and set them for use in a biorefinery.

Firstly, it is critical to address the material to be processed: lignocellulosic biomass and how they behave under microwave radiation. This can be reviewed as microwave effects on organic matter and polymers. Cellulose and lignin are examples of both aspects and have been studied to varying degrees, as separate materials and as biomass mixtures that are also found in natural abundance. Also the heating aspects of microwave can be related to thermal characteristics and information obtained from TGA data analysis. Microwaves are capable of heating objects volumetrically, and thus there is need to understand how and why this can occur in biomass and lignocellulosic materials. With consideration of selective heating, water would precede other substances presented in this study, and would have preference in microwave absorption over lignocellulosics and release more of that energy as heat losses due to having a higher dielectric loss tangent (**ε''**) and constant (**ε'**). However, this involves specific scenarios which include the microwaves being dampened as they pass through the biomass sample which is explained by the penetration depth (**D_p**) of microwaves, derived from the Beer-Lambert law and presented below as Equation 2.3 below:

$$D_p \approx \frac{\lambda_0\sqrt{\varepsilon'}}{2\pi\varepsilon''}$$ **Equation 2.3**

The penetration depth is obtained from the equation that focuses the incidental power decay as microwaves pass through a material (Equation 2.4), where **x** is the depth from the materials surface, **Q_0** is the incidental power and **Q** in this equation is the resulting power at that depth.

$$Q = Q_0 e^{\frac{-x}{D_p}}$$ **Equation 2.4**

According to Angela & d'Amore, this leads to bulk heating of the material and consequently would lead to a thermal effect on the surrounding matter (2012). This thermal effect can be determined based on the equation presented below (see Equation 2.5), it is key to observe that the solution **Q** or the Quality Factor in this equation, which is the microwave energy that is converted into thermal energy per unit volume, is heavily dependent on the dielectric loss (**ε''**) of the material within a specific electric field (**E** in V/m, and is the representation of applied microwave voltage in a given space and $\boldsymbol{f}$ is the generated microwave frequency).

$$Q = 2\pi\varepsilon_0\varepsilon'' f E^2$$ **Equation 2.5**

The same study also examines the dielectric properties of fruit and vegetables, however the concern remains that this perspective is focused on the moisture content of foods that contain significant amounts of moisture. It is also interesting to note the effect ionic particles have on the dielectric properties of water, decreasing dielectric constant and increasing loss factor of the solution. This could encourage the usage of sea water as an alternative solvent for processing biomass. Sahin & Ay suggest that the change in dielectric properties can be used to potentially determine moisture content and density of woody material, which seems plausible given the observable effects (2004). This information is useful but not in the full context of this thesis, however it could be proven otherwise upon development with biomass.

2.7. Dielectric Properties of Biomass

There is a potential benefit to exploring the dielectric properties of biomass, especially for processing date pit biomass with microwaves. In addition to the aforementioned studies revolving specifically around microwave interaction with cellulose and lignin, it is rudimentary to understand how biomass as a whole is affected by microwave treatments. A review of studies is necessary to observe these interactions, and to list processes that were tested and identify their purpose, choosing and optimising them for the purposes of this research thesis.

Aside from composition and density, it was made evident in another study that biomass dielectric properties are thermally dependant, with ε’ increasing up to a peak then declining and ε’’ decreasing overall (Navarrete et al., 2011). This is in agreement with another study by Sait and Salema using date palm biomass, where the movement of free water and potential structural changes influence the dielectric properties up to 200°C (2015). The same study has shown using the cavity perturbation method the exact behaviour of date pit dielectric properties: with dielectric loss (ε’’) at 2.45 GHz starting relatively high at 0.3 – 0.4, decreasing then spiking to <5 when it has charred (refer to Figure 2.4**Error! Reference source not found.**). Navarette et al. also employ the cavity perturbation method for measuring dielectric properties versus temperature; this will be expanded upon later as a useful method to determine the properties of the raw Khalas date pits used in this study.

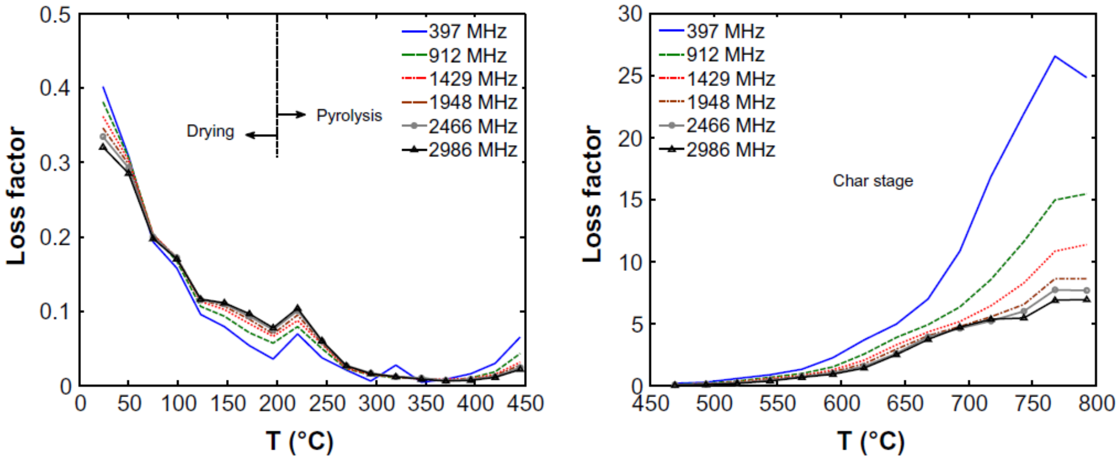

Figure 2.4 Visual data showing the dielectric loss of date pits versus increasing temperatures (Sait & Salema, 2015).

Upon continued review of studies on using microwaves to process biomass, the use of microwaves to remove woodworms from art pieces as a driving force behind a study is a good example to examine (Olmi et al., 2000). The purpose of this study is to observe the behaviour of microwaves in wood, and the changes in dielectric properties over different wavelengths. It is made evident that across several wood species that an increase in ε’ and ε’’ is attributed to increasing moisture content, which can vary in nature based on climate and soil conditions. It should also be that this is a slight decrease over the frequency range from 2 to 3 GHz, indicating the potential to use industrial grade equipment to process biomass. Sahin and Ay delve further into researching the relationship between water, biomass and dielectric properties; focusing on the potential of wood as structural material in electromagnetic fields (2004). Their research also shows two key points: 1) despite random composition, the dielectric properties of wood are dependent on the longitudinal and transverse directions, influenced by cellulose and lignin respectively; and 2) the dielectric properties are proportional to the density of biomass. The second point is more relevant to this research thesis as it would be difficult to organise the directional positioning of date pits in most processes, but their densities would fall within expected ranges depending on their cultivar and variety. However based on proximate analysis studies of date pits, their low moisture contents (roughly 5 % (Sait et al., 2012)) relative to these researched materials (0 - 28%) may pose a hindrance to microwave radiation processing methods. The addition of water, a significantly lossy material, should increase the dielectric properties of the biomass samples (Ellison et al., 2017), as well as the addition of biochar which also greatly increase dielectric properties when mixed with raw biomass in certain proportions. As the research shows a significant difference between 100% and 75% biochar, it is clear that the formation of biochar would in theory accelerate the pyrolysis of biomass mid-process under microwave radiation. So to the benefit of this thesis, it would be advantageous to design a method that would implement the strengths of water while controlling the acceleration factor caused by biochar formation.

The advantages of using microwaves based on this information include the volumetric heating of biomass and simultaneous formation of small hot spots that would quickly pyrolyse the biomass. This quickness can help induce faster pyrolysis speeds that can help generate higher bio-oil yields while minimising the charred areas based on how quickly the dielectric loss forms in charred date pits. By taking advantage of the charred areas heat loss, the bio-oil yields can be obtained quickly as well as potentially in larger quantities in comparison to conventional pyrolysis.

The conclusions drawn by the examination of preceding studies are also affirmed in a study by Paz et al.; moisture content, bulk density and temperature influence the dielectric properties which dictate behaviour of biomass during microwave processing (Paz et al., 2010). If combined with information obtained by Sait and Salema, where they observe more closely the effects of temperature and frequency on the dielectric properties of date palm biomass (not the seeds), it is noted that the water contained in the biomass is a key influence in pyrolysis up to 200°C (2015). Beyond that, pyrolysis would be attributed to structural changes occurring within the biomass as they absorb more energy, as well as the formation of biochar. This information will provide key points to look out for when designing strategies to pyrolyse hemicellulose; degrade cellulose in a controlled manner and liberate lignin for both to be used as feedstocks for prospective refining.

2.8. Microwave Biomass Processing

Building from the previous section, and moving toward the scope of this thesis, processing biomass using microwaves is still a novel methodology that needs further examination. While the general consensus of microwave usage is that it is a fast heating method/technique, there is still speculation that other effects occur or that the heating mechanism can be controlled and optimised to be able to draw out the potential benefits from processing biomass.

So under these assumptions, many of the conventional methods discussed in 2.5 can be combined. This can be achieved by using the information examined in sections 2.6 and 2.7 and then using these methods to observe special effects that occur because of microwave influence on biomass.

With regards to microwave pyrolysis, the subject has been studied very recently as a novel method with many unknowns as to the direct effects of microwave radiation on biomass, beyond the effect it has on the moisture content of said biomass. A study by Robinson et al. has more recently delved into figuring out what takes place during microwave processing of “dry” biomass (Robinson et al., 2021). With a keen interest in the formation of sugar based molecules (levoglucosan and furfural), the research shows that they are more readily formed in microwave pyrolysis than in conventional heating. Their formation adds to the difficulty of controlling temperatures within biomass as furfural is microwave sensitive and thus can lead to sudden thermal runaway, especially if the surrounding biomass has been thoroughly carbonised and likely to cause arcing. Despite the minor threat of hard to control micro-conditions, the benefits far outweigh the drawbacks. Examples of valuable resources taken from biomass pyrolysed by microwaves include H_2 gas, biomass with increased heating values and low weight bio-oil filled with sugars and aromatics (Huang et al., 2016). Bio-diesel has also been shown to be producible from microwave assisted pyrolysis, researched in detail by Nomanbhay and Ong (Nomanbhay & Ong, 2017). This can be made possible in conjunction with research outlining the pathways of lignin breakdown using microwave energy (Shaveta & Singh, 2014). Dry microwave pyrolysis is presented as a useful technique for this study, since by softening the date pits in this quick manner, valuable by-products can be generated for further treatment.

While dry microwave assisted pyrolysis is the main consideration of this chapter, hydrothermal microwave pyrolysis should be considered as a potential environmentally friendly method. Some of the effects that are known to occur to water under microwave radiation include:

- Rapid heating and generation of a pressurised subcritical fluid.
- Rapid dissociation of water molecules. Producing radicals and ions that make water simultaneously acidic and basic, and an ideal ionic liquid (Vaks et al., 1994).
- Significant drop in dielectric properties, leading to microwave transparency at higher temperatures. This allows for the microwaves to directly impact the processed material (Meredith, 1998).

The potential benefits of hydrothermal microwave pre-treatment are outlined in several studies, revealing the capability of this method to treat, depolymerise and carbonise lignocellulosic material (Guiotoku et al., 2009; Fan et al., 2013; Elaigwu & Greenway, 2016). Thus, it would be to the benefit of this study to look into usage of hydrothermal microwave treatment as a softening technique for the date pits and extraction of other valuable streams.

Based on the information gathered and reviewed on the challenges, benefits and methodologies for processing date pit biomass, this study can move forward using specific measures to generate the most value from the waste feedstocks. This study will focus on the use of microwaves to fast pyrolyse and hydrothermally pyrolyse date pit biomass, which will be used as an easily movable and replaceable biomass feedstock representative of the Middle Easts' agricultural waste outputs.

2.8.1. Cellulose

Fan et al. studied microwave interactions with cellulose, using a hydrothermal method where water is used as a microwave absorber and thus a heating matrix to hydrolyse cellulose (Fan et al., 2013). It is observed that microwave heating has a significant impact on the hydrolysis of cellulose; due in part to the thermal effects generated that affect the hydrogen bonds ensuring the stability of the cellulose structure. The primary objective of this study was to target cellulose (refer to Figure 2.5**Error! Reference source not found.**), and effectively convert it into glucose, which was observed to have significant preference of formation (Fan et al., 2013). However, not all the cellulose had converted as there were structures that require temperatures greater than 220˚C to affect them, but this method has been shown to be more effective than conventional methods. This is especially evident when combined with ionic liquids to produce greater selectivity in glucose production (Huang & Fu, 2013). Conventional methods that have been studied by Onda confirm the viability of hydrothermal hydrolysis of cellulose into glucose (2012). The use of catalysts to selectively convert cellulose into glucose is studied here, while also examining the impacts of other variables such as processing time and temperature, which impacts the stability of the glucose yield, and balling the raw material, that affects the crystallinity of cellulose which in turn affects the solubility and hydrolysis of cellulose. Guo et al. have also reviewed multiple other studies that have examined different pre-treatment methods such as the impact of solvents such as ionic liquids under microwave radiation, which have been shown to dissolve cellulose effectively (2012). Aside from the indirect thermal effects, Sahin & Ay have identified the reason cellulose structures are not affected by microwaves because they are bound by valence forces, preventing the influence of the electric field on present dipoles (2004). That is to say that cellulose is microwave transparent in comparison to water and hemicellulose pyrolysis products that would have formed from being in close proximity to trapped superheated water, and will thus not be heated directly by microwaves. By understanding how one of the main constituents of lignocellulosic material is effected by microwave energy, cellulose extraction and conversion can be predicted and determine how it would impact the remainder of the biomass. This will allow better designing processes for optimised refining of lignocellulosic biomass.

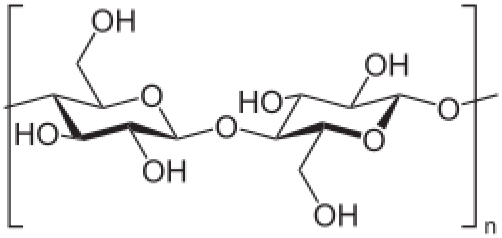

Figure 2.5 An example monomer unit of cellulose (Nishiyama et al., 2002)

2.8.2. Lignin

The second most abundant natural polymer, lignin, is relatively more resilient than cellulose, and has been studied at length to use it as an abundant source of biofuel and materials due to the aromatic structure of lignin and its monomers (seen in Figure 2.6). Most research on lignin however centres on harsh processes including high power microwave processing. Microwave interactions with lignin and subsequent behaviour that may occur in some of these processes, perhaps showing different characteristics despite lignin lacking polarity and being large therefore potentially being limited to undergoing thermal effects.

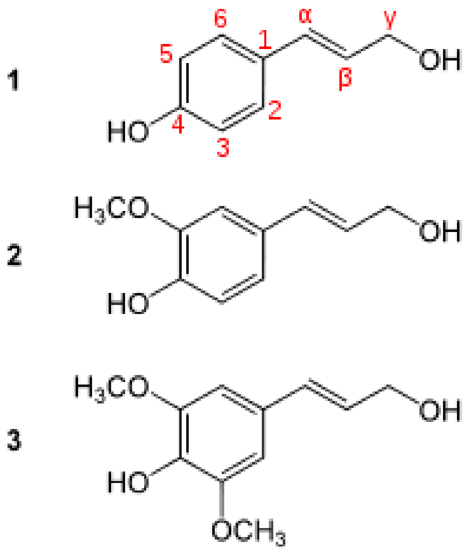

Figure 2.6 Lignin monomers: 1) paracoumaryl alcohol (H-lignin), 2) coniferyl alcohol (G-lignin) and 3) sinapyl alcohol (S-lignin).

Among these studies, Zhou et al. has reviewed several pieces of research that investigate the use of microwaves to extract lignin, studies that essentially take advantage of lignins thermal resilience to separate it from biomass (Zhou et al., 2017). These studies indicate the potential for high yields and high purities using microwave energy, and relying on thermal stability of acidolysis lignin in comparison to conventional methods at 190˚C. It is hypothesised that H_2SO_4 ions in solution are directly affected by the electromagnetic field and react more quickly and intensely. It is unfortunate that although there are many studies that investigate thermal effects (conventional or microwave) on lignin, there is very little research describing other direct microwave effects on the biopolymer. However, the available information can be used to detail the likely products from microwave assisted processing of lignin. More information may be gathered from future work conducted through this study.

2.9. Commercial Feasibility of Biomass Processing in Oman

The use of date pit biomass would become a relevant industrial platform for the Sultanate of Oman as it is one of the leading agricultural products and carries significant social value in the region. This section examines the feasibility of implementing biomass processing facilities in Oman, positioning around date pits and palm biomass. Furthermore, concerning the petroleum-based economy and infrastructure of Oman, date pits will be considered an alternative and supplementary fuel and economic source. By exploiting them to boost and fortify against future financial struggles and add to the growing portfolio of renewable resourcing after solar and geothermal energies in Oman.

This section will discuss two of the many products due to the diversity of the potential outcomes of biomass pyrolysis, as seen in section 2.4.4. Lignin is a priority as it is within the scope of this study; the cost of the lignin biopolymer is tied to its extraction and purification processes as well as its molecular weight (Ľudmila et al., 2015). One of the most common and commercially available lignin is Kraft lignin which is obtained as a by-product of the paper-making industries and is usually priced at 260-500 USD/MT (Gosselink, 2011). Lignin can be a versatile platform chemical to produce other viable polymers. This study is under the pretence of extracting lignin in an environmentally benign and less destructive manner than chemical extraction (with a market price of up to 520 USD/MT for organosolv lignin, considered to be a highly pure form of lignin) (Gosselink, 2011). Thus Oman and the Omani agricultural sector would be producing an additional and fruitful revenue stream worth at least 3.9 million USD annually based on low purity lignin obtained from date pit waste alone. This implementation's technological impact and growth can expand into other biomass waste sectors to bring about a socio-political change in how the region treats valorisable waste. By extracting value from all of the agricultural waste in this way, the overall contribution to the gross domestic product (GDP), a potential of up to 15 million USD assuming the biomass waste (constitutes 5% of overall waste in Oman) contains up to 30% as lignin (Qazi et al., 2018) and employment growth has the prospect of benefiting from this one product stream alone.

Bio-oil is another primary product that this section should highlight and is generally obtainable from fast pyrolysis of most biomass. Regardless of whether the processed material has had its lignin removed or not (this primarily changes whether the bio-oil contains phenolic content), it would still have cellulose reserves that can produce suitable quantities of carbohydrate-rich bio-oil. Freshly made bio-oil is usually not used as a fuel but rather refined into bio-diesel (Abu-Jrai et al., 2017) or bio-ethanol (Binder & Raines, 2010) depending on the source and composition, generating 43.24 and 29.8 MJ/kg respectively upon combustion. For example, levoglucosan is a typical product of biomass pyrolysis, found in refined bio-oil and usually hydrolysed into fermentable glucose, which then leads to bio-ethanol that burns relatively cleanly. While bio-ethanol is a significantly cleaner alternative, Oman's desalination plants and oil refineries could benefit greatly from the energetic combustion of bio-diesel as a replacement to natural gas. These process/industries typically use natural gas (52.2 MJ/kg) to power local settlements while producing potable water and refining crude oil. So using locally produced bio-oil to supplement these industries can benefit the country economically and environmentally while offsetting the carbon impact of these processes. The softened bio-char residue, another by-product of fast biomass pyrolysis, can also be used to extract remaining valorisable phenolics or as a precursor to activated carbon that can be used to clean the exhaust and waste streams from the industries (Park et al., 2013). Overall, the pyrolysis residues of date pits can become a significant financial boon to the Sultanate of Oman and open doorways to process other forms of agricultural waste in the country and its neighbours.

With regards to the fast microwave pyrolysis process, since solar energy can power microwaves effectively and renewably, Oman already has systems to expand in this sector via the growing solar power generation industry. As a country with plentiful amounts of solar and thermal energies, there is a prime opportunity to process date pits and other agricultural biomass waste materials renewably. Some future solar power contributions are expected to produce 450 MW of power in the capital of Muscat alone (Kaleem, 2022) which can save the country 2 million USD in electrical subsidies. These economic benefits can be increased by coupling them to microwave-based refinery processes. Meanwhile, the infrastructure to collect and consolidate biomass waste is being developed by funding projects such as Maana by be'ah, which exists to help manage large garden and farm waste to be recycled or discarded in designated zones (Oman Environmental Services Holding Co., 2017). TGA and Py-GC/MS can also enable the discovery of other pyrolytic pathways that can lead to new processing routes and product streams (Chen et al., 2019). For example, abundant salt water can facilitate new desalination methods using the activated carbon product and potentially open doors for hydrothermal processing using seawater (Ren et al., 2016). By relying on and improving current services and capabilities to feed into the biomass industry, Oman can develop further to obtain a reliable economic platform and enhance environmental protections and renewable benefits in the Middle East.

3. Methodology

The methods used to obtain the information kept within the date pits are outlined in this chapter. As they were justified in the previous chapter, the following methods have been adapted to be used in the researchers work environment within safety and equipment restrictions. These methods may be used in the coming chapter to analyse the products of this study's processing techniques.

3.1. Raw Sample Acquisition

The samples were acquired from local (Oman) farms and market, making sure to obtain the same variety (Omani Khalas variety) of date palm fruit. The seeds and pits were then collected post consumption from several houses, sun dried in 40+ °C, washed and dried overnight at 60 °C in an oven for 48 hours before being used in analysis and processing. The date pits were then "skinned" to physically separate the brown seed coat (skin) from the white/translucent endosperm (core) using a scalpel. The volume of the date pits was measured by displacement and by measuring the dimensions to get an average value of ~ 0.7 mL, leading to a density range of 930 – 950 kg/m^3.

To observe the effects on cellulose in particular, α-cellulose (purchased from Sigma-Aldrich) was used as a representative. Since it is commonly used to observe the behaviour of cellulosic enzymes, it will serve its intended purpose suitably for this study.

3.2. Analysis Methods

The analysis methods presented below will initially be used to valorise the raw materials. The methods that will be used to analyse the processed materials will be the proximate analysis method for energy and lignin content; point load tests for crushing force; Py-GC/MS for pyrolysate content of the process yields. The illustration below (Figure 3.1) is a brief outline of the analytical methods used on the test samples before and after processing, outlining the analysis pathways and expected result data sets.

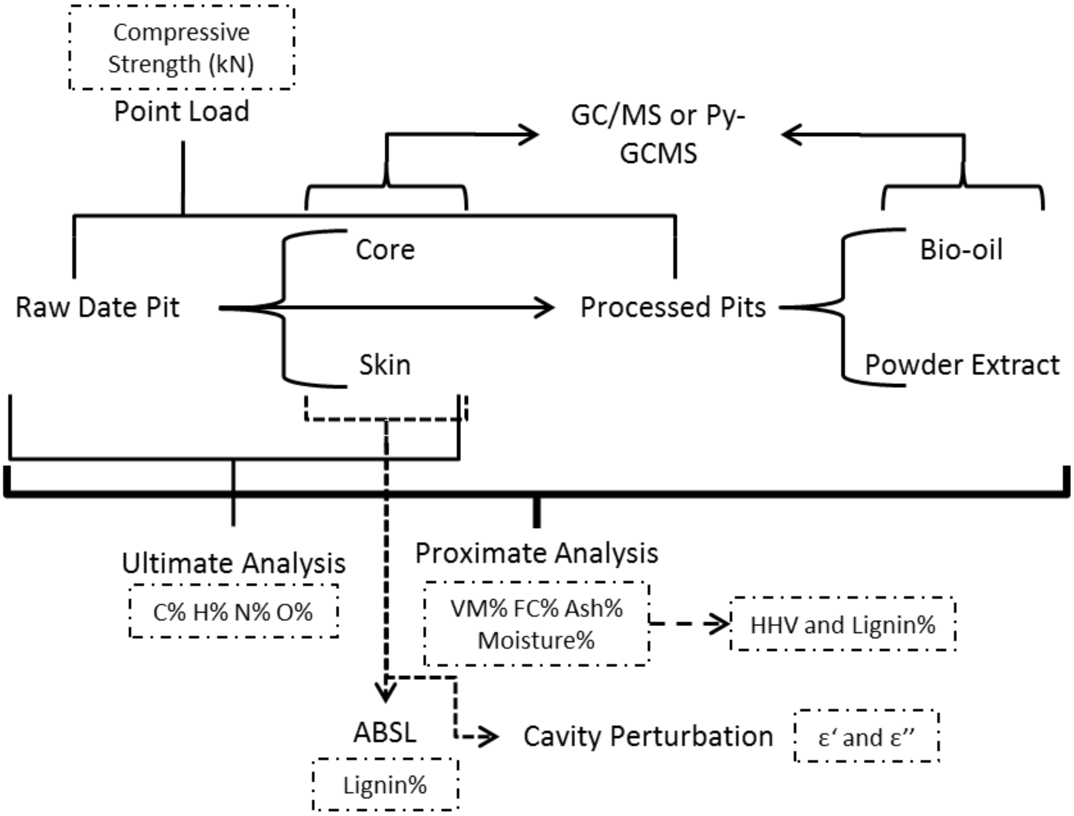

Figure 3.1 Outline of analytical methods used in this study.

By subjecting the date pit samples to the aforementioned analytical methods, GC/MS can predict the pyrolysis products, and ultimate/proximate analysis can estimate the fuel potential of the raw material. Py-GC/MS and TGA can also determine the pyrolytic pathways and the degradation points of the date pit components. ABSL combined with TGA estimates can also resolve the quantities of extractives such as lignin, giving a better idea of how to approach the date pit biomass in terms of processing conditions for this study. Overall this is to fulfil several criteria of the objectives of this research study, to characterise the date pits as viable fuel replacement and renewable source of platform chemicals.

3.2.1. Ultimate Analysis

Ultimate analysis was performed using the LECO TruSpec Micro CHN analyser at the University of Nottingham. Sulphur content was expected to be negligible as the samples were pure biomass and expected to have little exposure to sulphur during transfer and analysis.

3.2.2. Proximate Analysis

Proximate analysis was performed using the TA Instruments Q500 TGA. The TGA method was adopted by combining the methodologies of several studies (Sanchez-Silva et al., 2012; Sait et al., 2012; Babiker et al., 2013; Nasser et al., 2016) and adjusting them to provide as much detail as possible. The TGA profile was arranged as such: Under inert nitrogen gas flow with flow rate of 100 ml/min to maintain pyrolysis conditions. With initial temperature at 30 °C, temperature was ramped at 10 °C/min to 110 °C and held for 10 minutes, measuring the mass loss associated with moisture. The temperature was then ramped at 5 °C/min up to 600 °C to obtain a good resolution in the Differential Thermal Analysis (DTA) in this region. The rate was then increased to 10 °C/min up to 900 °C, thus obtaining the amount of volatile material present in the sample. This temperature was held for 15 minutes, before switching to oxygen gas flow rate of 100 mL/min for 10 minutes to ensure complete combustion. From this result, the fixed carbon content and ash content is acquired.

3.2.3. Acetyl Bromide Soluble Lignin Analysis

Acetyl bromide soluble lignin (ABSL) was used as a rapid lignin quantification method using a modification of the method described by Fukushima and Hatfield (2001). 100 mg of samples were incubated with 4.0 mL of 25% acetyl bromide solution in glacial acetic acid at 50 °C for 2 hours. After cooling, the volume was made up to 16 mL with glacial acetic acid and left to settle for 30 min. 0.5 mL of this solution was further diluted with 2.5 mL of glacial acetic acid and 1.5 mL of 0.3 M NaOH and mixed by hand agitation. Then, 0.5 mL of 0.5 M hydroxylamine hydrochloride solution and a further 5.0 mL of glacial acetic acid was added and the absorbance was measured at 280 nm (7315 spectrophotometer; Jenway, Stone, UK). Lignin concentrations were calculated using extinction coefficient generated from corresponding measurements using Kraft lignin standards purchased from Sigma-Aldrich prepared in concentrations of 0.4, 0.6, 0.8, 1.0 and 1.2 mg/10 mL.

Extinction coefficients were calculated from standard curves as follows: 10 mg of isolated lignin (after corrections for carbohydrate and protein contaminants) was dissolved in 5.0 mL of dioxane, and aliquots of 0.2, 0.3, 0.4, 0.5, and 0.6 mL were pipetted into separate tubes. 0.5 mL of 25% acetyl bromide in glacial acetic acid was added to each tube. Tubes were tightly capped (PTFE-lined caps) and put in a 50 °C water bath for 30 min. After cooling, all tubes received 2.5 mL of acetic acid, 1.5 mL of 0.3 M NaOH, and 0.5 mL of 0.5 M hydroxylamine hydrochloride solution. Tubes were shaken and acetic acid was added to make up a final volume of 10.0 mL. Solutions were analysed in a spectrophotometer at 280 nm.

3.2.4. Point Load Tests

This method was used to obtain a representative evaluation of how much force would be required to initially fracture/grind a date pit sample. The apparatus used was a Digital Point Load Test Apparatus 77-0115. The sample was placed in 2 different orientations (on its sides and with a point within the furrow/groove, as indicated in Figure 3.2), and analysed in triplicate for each orientation. The data points were averaged to obtain an inclusive value of the whole date pit, under the expectation grinders or blenders would contact these two areas most of the time.

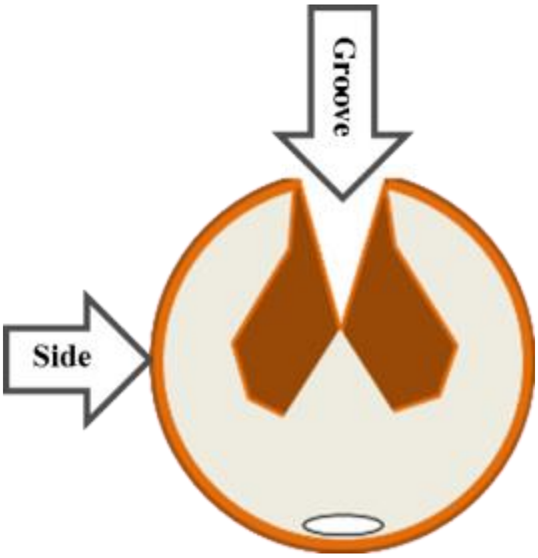

Figure 3.2 An illustration depicting the orientation of the point load tests.

3.2.5. Dielectric Analysis/Cavity Perturbation Method

The cavity perturbation technique was used to measure the dielectric properties of the date pit raw material, and was adapted from the method as described by Navarette et al. (2011).

The samples (< 0.05g) were loaded into quartz tube (3 – 7 mm in diameter) and filled to about 1 cm in length and packed as densely as possible. The tube was then attached to the sliding sample holder, where the sample was analysed by an HP 8753B vector network analyser. The sample would then be raised into an attached furnace to observe dielectric changes caused by temperature. The samples were heated in the furnace and held for 2 minutes, then lowered at set temperatures for dielectric measurements. The tubes were not sealed due to the expected formation of high pressure volatiles and high temperature conditions (30 – 600 °C). Below (Figure 3.3) is a representation of the apparatus, as seen in (Navarrete et al., 2011). The samples were analysed under 2.45 GHz as most of the processing equipment uses this frequency and to represent the conditions of industrial microwave frequencies.

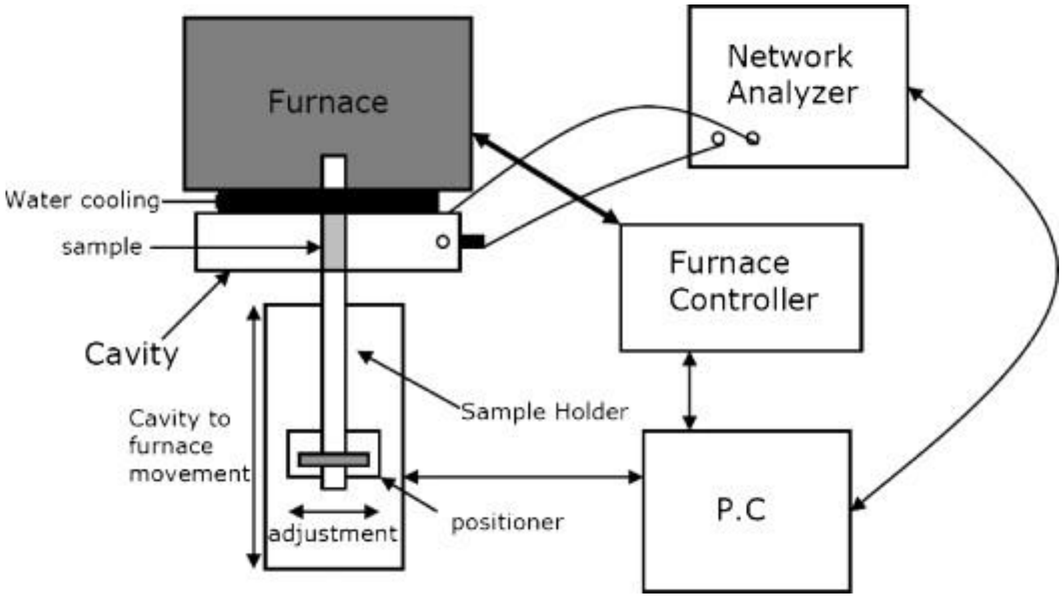

Figure 3.3 A representative diagram of the apparatus used to analyse the dielectric properties of the date pit biomass (Navarrete et al., 2011).

The main issue of this method is that the volatiles would evaporate with no safe way to contain them in liquid state or keep them under pressure. There is also the issue of not obtaining real-time analysis of pyrolysis effects on the dielectric properties of solid biomass, though this is known to be a difficult aspect to overcome. Therefore there would be little information on the dielectric effect of the volatiles on the biomass as a whole.

3.2.6. GC/MS and Py-GC/MS

GC/MS analysis will be used primarily to study the liquid products of the processes, while Py-GC/MS will be used for solid products. It should be noted that the solid products will be flashed pyrolysed and therefore will need to be interpreted through their pyrolysates (e.g. Lignin will produce catechol and phenols), while liquid products will be dissolved and the solvents may interact will biomass in unlikely but unexpected ways, showing a significant component where there isn't one.

It is important to note that the exact quantities are of particular interest, and even then it would be difficult to standardise for the Py-GC/MS results due to the method not allowing space to place internal standard. However this is counteracted by the fact that whole undiluted samples are analysed and thus, the relative peak areas can be used as a reference point to approximate quantities in otherwise complex mixtures.

Another drawback to Py-GC/MS is that, since several very light molecules (H_2O, CO_2, light alcohols and acetic acid) are pyrolysis products of lignocellulosics, the adapted methods do not take into account the measurement of these compounds and can skew the obtained results as it is expected they are produced in significant quantities during the early stages of pyrolysis.

For GC/MS, if the bio-oils had low enough viscosity that they could be dissolved in a DCM/Methanol solution for analysis. This solvent mixture was necessary as to ensure all bio-oil components were dissolved and could be sent into the GC.

A GC Method was adapted from literature to ease identification of the pyrolysates based on collected information (Subagyono et al., 2016; van Erven et al., 2017; Hidayat et al., 2018). The GC oven was held at 45 °C for 5 min, then heated to 270 °C at 5°C/min and held for 5 min. With the flow rate of the carrier gas set to helium at 50 ml/min with 20:1 split ratio for the GC/MS samples and 50:1 split ratio for Py-GC/MS samples. Separation was carried out using an Agilent Technologies HP-5MS Inert column (5% Diphenyl / 95% Dimethylpolysiloxan ; 30m, 250 µm inner diameter and 0.25µm film thickness) While quantitation is encouraged for most scenarios, the main objective of this method is qualitative analysis using AMDIS by NIST, with relative quantities used as a comparative indication of lignin amounts.

Approximately 0.5 – 1 mg of sample was inserted into 1 mm diameter quartz tubes. The tubes were then inserted into the pyrolyser. A CDS 1000 pyroprobe/pyrolyser was coupled to an Agilent 7890B/5977A GC/MSD system with a heating rate of 20 °C/ms, up to 500 °C. The pyrolyser was then purged by helium (99%) into the GC via a preheated (270 °C) transfer line, with a flow rate of 50 ml/min. The inlet temperature was set to 230 °C. The chromatograms were analysed using the Automated Mass Spectra Deconvolution and Identification System (AMDIS) by NIST. Comparison with literature allowed for identification of fragments. Quantities were calculated by calculating percentage areas for each pyrolysate. The analyses were used to interpret the raw material and experimental processing results.

3.3. Processing Methods

3.3.1. Hydrothermal Microwave Extraction

The apparatus used for this process was the Anton Paar GmbH Monowave 300. 15 mL of distilled water was poured into a 30 mL quartz vial, after which a number of date pits (1 – 7, 0.03 – 0.07 g/mL) were put in. The vials were then subjected to 850W of microwave radiation up to the required temperature with some radiation occurring to maintain the temperature (~15W). Changing the mass ratio was to observe the effect of mass on hydrothermal microwave extraction (HME), as well as considering the difficulty in consistently matching the mass of date pits per experiment. Consistency was instead focused on the number of seeds in the reaction vessel. The vials were then inserted into the Monowave and experiments were run to observe the effects of time (5 – 60 minutes) and isothermal temperature (150 – 180 °C) on the extracted yields and processed date pits. This experimental range was selected to observe the effect of time and temperature on extract yields, as well as in consideration with apparatus safe use limits when using water as the base solvent (~200 °C, 30 bar) with experimental pressures capable of reaching 15+ bar.

The contents of the vial were then decanted into centrifuge tubes, while the solid date pits were taken out and set on glass plates. The plates were put into a drying oven at 60 °C overnight, while the centrifuge tube was put in a centrifuge for 30 minutes at 3200 RPM. The fluids were decanted into 15 mL vials and stored in the oven for 48 hours to thoroughly remove all water. This is to capture the bio-oil yields. The solids that remained in the centrifuge tube were collected in 5 mL vials and dried overnight at 60 °C, as this is expected to be concentrated lignin extracts.

3.3.2. Microwave Pyrolysis

A custom microwave pyrolysis rig was connected to a SAIREM GMP 20K 2kW generator for this process. It was optimised to pyrolyse the date pits under an inert N_2 atmosphere (to minimise combustion) and to collect charred date pits and condensed bio-oil. A diagram of the pyrolysis setup is shown in Figure 3.4.

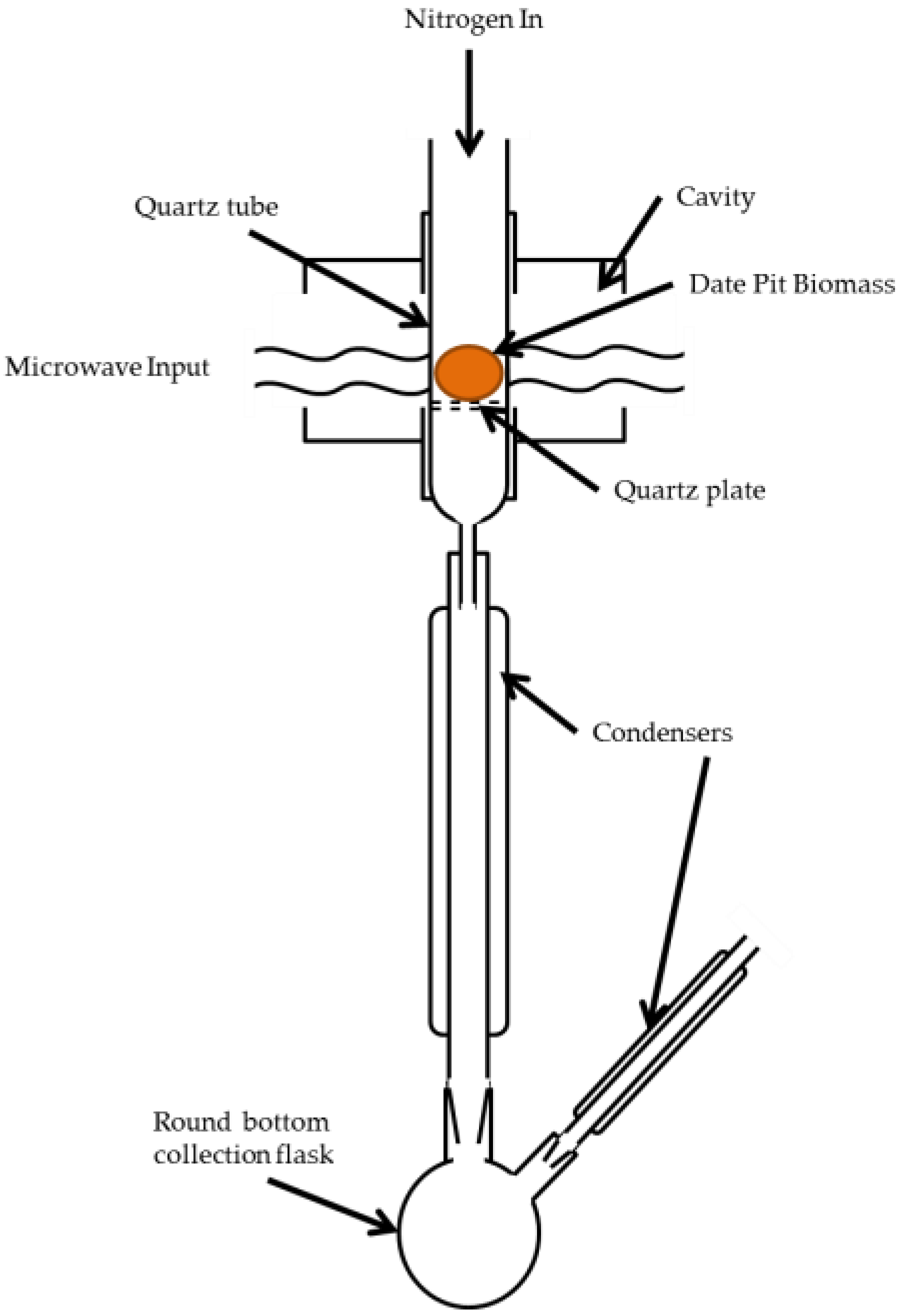

Figure 3.4 An illustration of the microwave pyrolysis rig, used to pyrolyse dry date pits to soften the date pits and produce date pit bio-char and bio-oil.

The reaction glassware was set up to optimise cooling the evolved gases post-treatment. The date pits were put into a quartz tube (3 cm diameter) to reach a height of ~3 cm (7 – 10 g), to ensure that the microwaves pass through the biomass. The quartz tube is placed inside a cavity with dimensions 8.5 cm x 4.5 cm x 10 cm. The quartz tube contains a plate to separate the solids and allow liquids and gases to pass through. Once the pyrolysates pass through the plate, they are carried by the N_2 gas (2.0 mL/s flow rate) into a condenser. The condenser leads into a round bottom flask with another condenser attached to capture excess volatiles. The flask is kept in a bucket of ice to further increase the bio-oil yield. This method will increase liquid yield while also potentially increasing H_2O contamination evolved from the pyrolysed biomass. The samples are freeze dried overnight to observe the amount of water and volatile components which contribute to the overall bio-oil yield.

This overall microwave set-up was used so that the date pits make use of the microwave pathway from the generator, the samples occupying enough space to emulate a packed biomass block sub-optimally. The evolved gases would then pass through two cooling sections to ensure that as much oil as possible is saved from extraction and carried by the evolved moisture. By capturing the water (formed as a by-product of pyrolysis), there remains the possibility of determining how much water forms from the dry biomass pyrolysis and increasing the capturing of the non-aqueous fraction, which can be purified later by drying methods such as freeze drying.

4. Results & Discussion

The results obtained from the methods outlined in the previous chapter. The outcomes, hypotheses and potential reasons for process mechanisms and product formations will be discussed.

4.1. Date Pit Characterisation Results

4.1.1. Ultimate Analysis & Proximate Analysis

For this study, samples of the date palm pit were divided into 3 components: Date Pit Whole (DPW) or the raw date pit, Date Pit Skin (DPS) and Date Pit Core (DPC) (refer to Figure 4.1). The results obtained using the outlined analysis methods are presented in Table 4.1. The average gravimetric mass of the Khalas date pits used in this study is 656 ± 140 mg, with the skin and core constituting roughly 15% and 85% of the overall mass respectively.

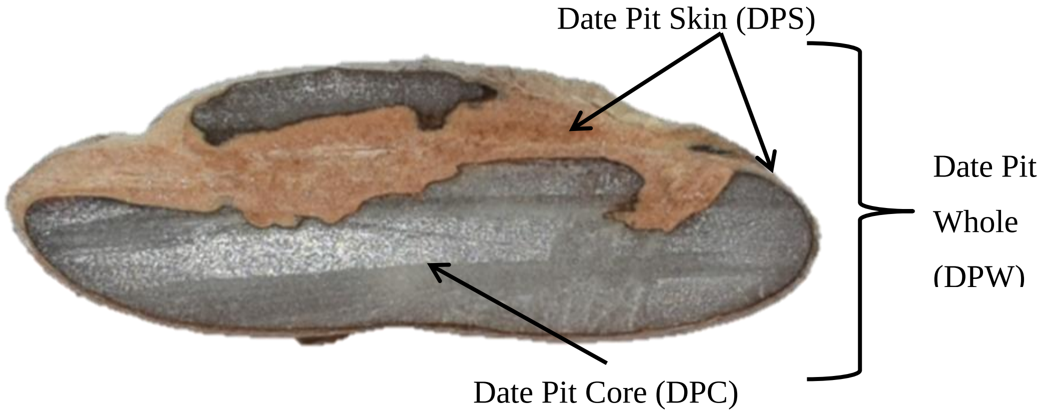

Figure 4.1 A cross section of a raw date pit, indicating the locations of the skin and core.

Table 4.1 Proximate and ultimate analysis of date pit components and other biomass from various studies for comparison.

Type	Ultimate Analysis[1]				Proximate Analysis[1]			Moisture Content	References
	C	H	N	O[2]	VM	FC	Ash		
Date Pit Whole	49.37	6.60	0.99	43.04	77.45	21.84	0.71	4.09	This study
Date Pit Skin	48.60	6.44	0.80	44.16	71.81	26.86	1.38	5.54	This study
Date Pit Core	45.74	7.45	1.12	45.69	80.71	15.66	1.63	6.63	This study
α-cellulose	---	---	---	---	91.74	7.48	0.78	6.14	This study

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[1] Dry weight % basis
[2] By difference

Olive Stone	49.00	6.10	0.80	42.00	78.30	19.50	2.20	---	(Cordero et al., 2001)
Date Palm Stone (Date Pit)	47.14	6.63	0.9	45.33	83.33	14.94	1.4	---	(Nasser et al., 2016)
Date Palm Trunk	44.46	5.75	0.55	49.24	78.53	17.61	3.86	---	(Nasser et al., 2016)
Brewers Spent Grain	53.50[1]	7.27[3]	4.89[3]	34.04[3]	79.22	16.46	4.32	---	(Olszewski et al., 2019)
Brewers Spent Grain	---	---	---	---	81.54	14.02	4.44	5.35	This study
Bituminous Coal	66.5	4.4	1.2	13.3	23.5	62.5	13.9	7.4	(Coppola et al., 2015)

One of the key points to note is the similarity of date pits to olive stones with respect to being a potential solid biofuel. When comparing the DPS to the DPC, the differences between the volatile matter (VM) and fixed carbon content (FC) can provide significant indications of several properties. A higher FC content is indicative of carbon that is bonded in states that are highly thermally stable such as phenolics. A substantial difference between the FC of DPS and DPC (26.9% vs. 15.7% respectively) combined with the relative closeness of their ultimate analysis carbon results (48.6% vs. 45.7% respectively) shows that despite having similar amounts of carbon, the fixed carbon content of the skin enforces the anticipation that thermally stable carbon is more present within the skin than in the core. While it is unlikely the skin and core can be separated, the DPS is seen to be a more beneficial fuel source than the DPC since it has more carbon and thus more combustible energy sources stored. The ultimate analysis is useful for determining other fuel characteristics such as clean burning, as a higher C/H ratio indicates that more carbon emissions are produced during combustion. Overall, when comparing the raw date pit C/H and its components with coal; it is evident that burning raw date pits would be more welcome in a more environmentally conscious setting as they would provide half the calorific energy with significantly fewer carbon emissions (also since growing the biomass fuel is a carbon neutral pathway).

It is essential to note the differences in composition between DPS and DPC. And despite not being listed, it should be known that the moisture content for all samples was in the range of 4 – 7% which indicates that date pits are relatively dry irrespective

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[1] Dry ash-free basis

of storage conditions. Another feature to note is the low ash content, which is a good indicator of how much energy can be cleanly drawn from solid biomass. Combined with low moisture contents, this can help reduce the transportation costs for moving biomass since more of it is usable.

Again addressing the fixed carbon compositions, it is observed that although there would be a lower overall quantity of DPS, there is a significantly higher concentration of fixed carbon than in DPC. This is an indication of higher energy content and higher lignin/phenolic content (Demirbaş, 2003). It can be theorised that the majority of extractable lignin is present in the skin sections of date pit or the brown areas as observed in Figure 4.2 and Figure 4.3. This is also based on visual observation as cellulose and starch are known to be colourless / white, while lignin is known to be red or brown in colour. The energy and lignin content will be extended upon in sections 4.1.2 and 4.1.3 respectively.

Figure 4.2 A longitudinal cross-section representation of a date pit (left) and a photo of the cross section (right).

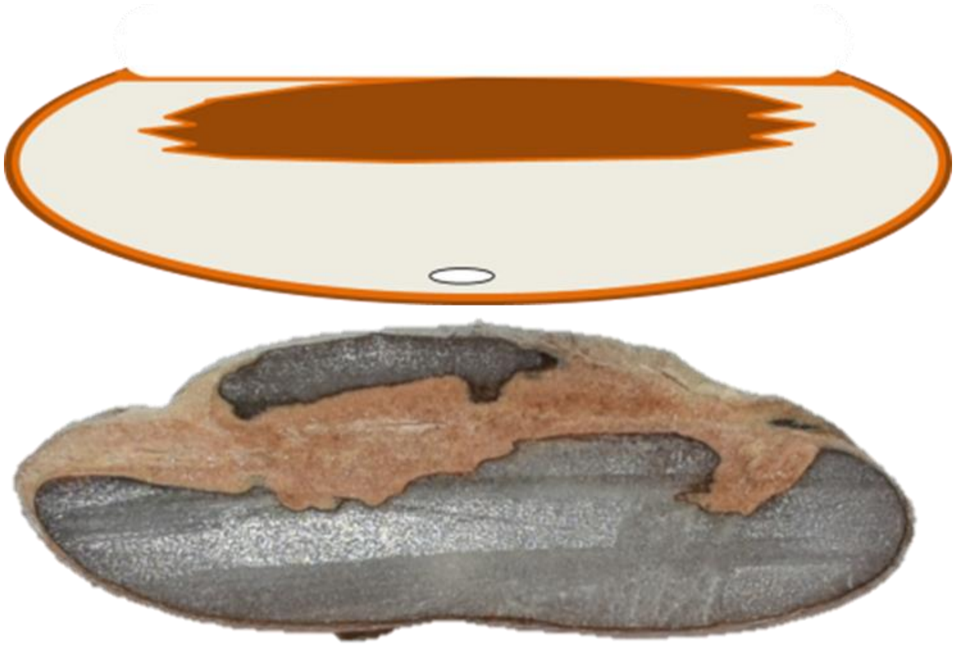

Figure 4.3 A latitudinal cross-section representation of a date pit (top) and a photo of the cross section (bottom).

As for the volatile matter, if compared to α-cellulose, the date pit overall has significantly less volatile matter; however, the DPC releases more volatile material and is comparable to a purely cellulosic sample. This might indicate polymers that pyrolyse and decompose readily below 500 °C, such as hemicellulose, starch and cellulose. This behaviour is expected as seed anatomy would suggest that the embryo requires an energy source to nurture it. This information is also valuable for designing methodologies limiting cellulose and starch's evolution and pyrolysis and potentially allowing hemicellulose removal and liberation of the lignin-rich skin from the cellulose/starch-rich core.

In reference to the TGA/proximate analysis methodology used for this section (see 3.2.2) with particular emphasis on the range between 110 and 600 °C, there are two important reasons why a ramp rate of 5 °C/min was used (see Figure 4.4).

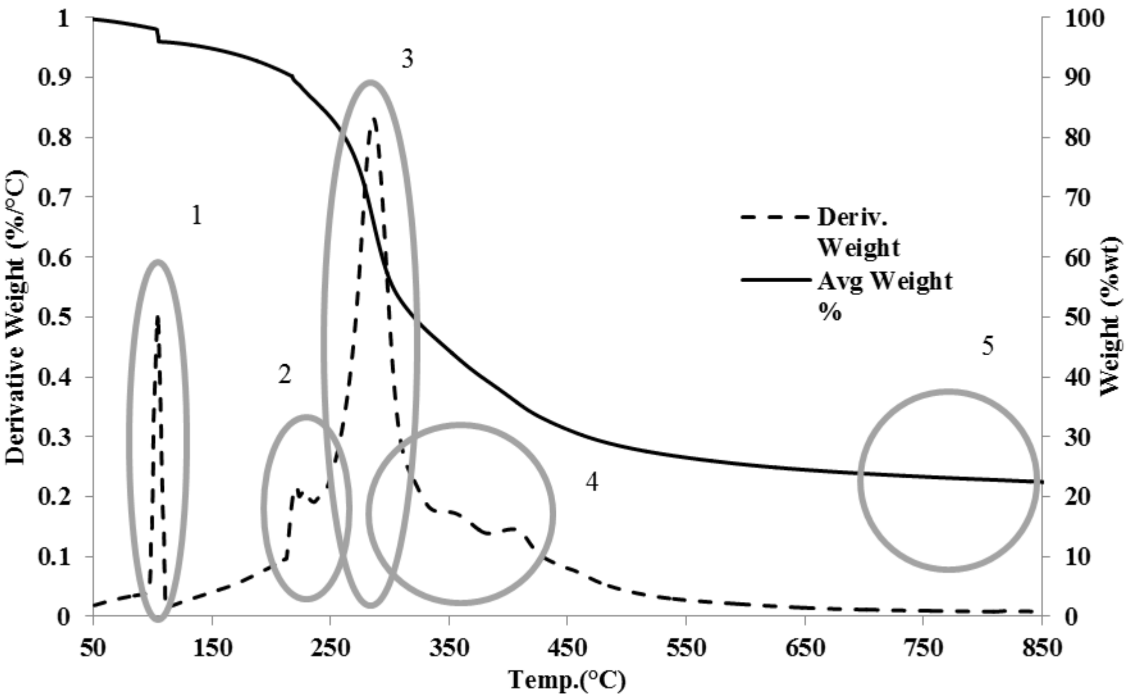

Figure 4.4 The TGA/DTA chart of DPW. The marked regions represent as follows: 1) the drying/moisture loss region; 2) the hemicellulose shoulder region; 3) the cellulose peak region; 4) the volatile lignin region; 5) fixed carbon region (Demirbas, 2004; Yang et al., 2007; Cheng et al., 2012; Babiker et al., 2013).

First of all, it will allow for good thermal conduction and heat transfer across the sample, thus enabling heat energy intake to spread evenly throughout the biomass with little inhibition. This can be observed in a study by Jiang et al. (2010) where they demonstrate the effects of varying ramp rates on the outcome DTA charts. It can be seen in this study that if the DTA curves are interpreted correctly, the larger peaks denote that more of a specific material is burning at a faster rate and the peak resolution becomes better. Secondly, due to the relatively even distribution of heat, the various components should pyrolyse closer to their peak degradation temperatures. Allowing the DTA peaks to resolve more sharply, larger and with less overlap, especially between the hemicellulose and cellulose peaks. An example of this application can be seen in Figure 4.5, comparing α-cellulose to the studied biomass. A-cellulose, which is essentially extracted cellulose in its longest polymeric chain form and prior to being made into paper, was used here to showcase the thermal stability of mostly pure cellulose relative to hemicellulose fractions in biomass (Pure cotton is ~90% α-cellulose). If the height of the peaks were relative to the concentration of cellulose present in DPC and DPS, this adds more evidence that the core of date pits is made up of significantly more cellulose/starch than the skin.

This method however does not apply as strictly to the resolution of lignin in the DTA charts as, due to the variable nature of lignin structures, it partially degrades between 200 – 500 °C with small low resolution peaks with a chance to reveal peaks above 500 °C. This can be observed in Figure 4.4, the 4th region that corresponds to the volatile lignin, thus reinforcing the hypothesis that lignin and its phenolic by-products contribute more to the fixed carbon fraction (5 in Figure 4.4) than the volatile matter region during pyrolysis.

Observation of the peaks positions and heights in the DTAs reveal key points about the biomass samples. Noticeably, depending on the peak locations within known ranges, the component contributing to that peak in mass loss can be identified. For example, cross referencing with experimental data and reported data (Singh et al., 2009), it can be inferred that the peaks observed in region 3 in Figure 4.4 represent cellulose, as cellulose has a degradation temperature within the range of 250 – 400 °C (Yang et al., 2007). Another observation the DTA chart is the effect components have on each other. That is to say, when the cellulose peak resolves as seen in Figure 4.5 below, then the presence of lignin and hemicellulose has skewed the peak to evolve at the lower ends of its degradation temperature range. This hints at the possibility that during pyrolysis the quantity of the cellulose majority can also be indicated by the peak height, resolution and area and thus be deconvoluted to obtain estimations. Or if there is comparison to be drawn between DPC, DPS and DPW cellulose concentrations, due to the reduction of other constituents such as hemicellulose, the cellulose can absorb heat more readily and pyrolyse sooner and faster, thus producing a relatively larger peak in its range.

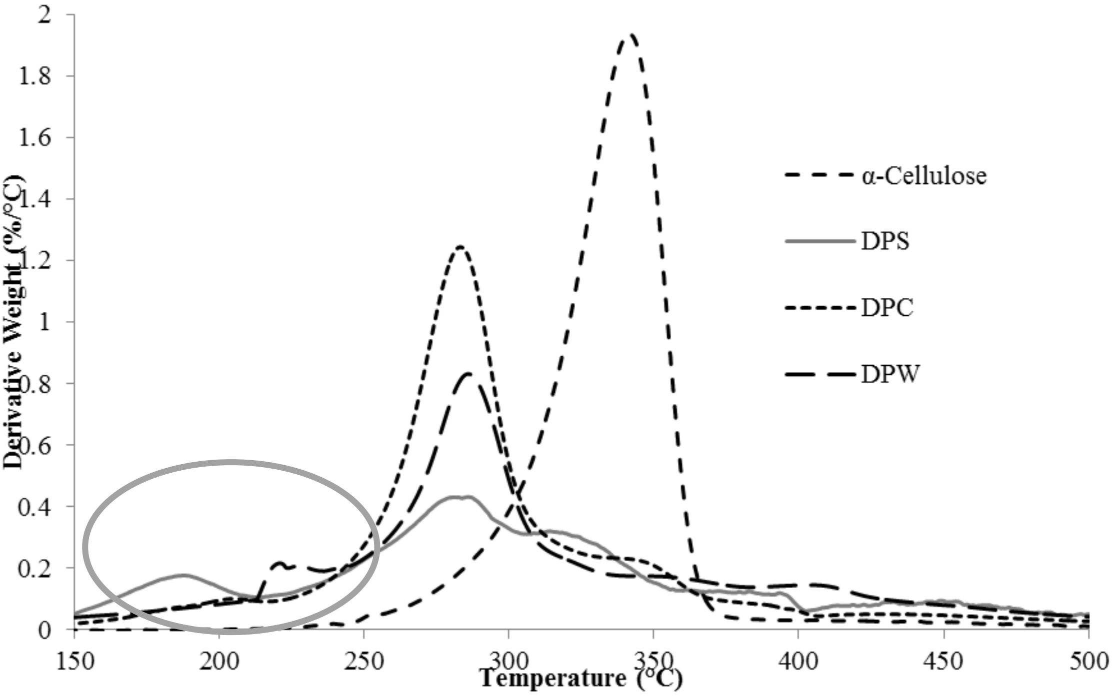

Figure 4.5 The Differential Thermal Analysis comparison between α-cellulose, Date Pit Skin, Date Pit Core and Date Pit Whole. The circled area is the approximate range for hemicellulose degredation.

The peaks that indicate where hemicellulose and cellulose evolve from the sample can be seen in the TGA/DTA of Date Pit Whole (Figure 4.4) in the regions marked **2** and **3** respectively. Several studies include temperature ranges where the peak weight loss from hemicellulose and cellulose degradation and pyrolysis occur (Yang et al., 2006; Yang et al., 2007; Singh et al., 2009; Sait et al., 2012; Sanchez-Silva et al., 2012; Watkins et al., 2015; El-Khaldi-Hansen et al., 2016); the information is used to ensure correct assignment of peaks is done. For this study, the assumption is made that peaks resolved in the range of 150 – 250 °C range correspond to hemicellulose degradation, while cellulose degradation peaks are likely to be found between 200 – 500 °C. Another assumption to have before analysis is that higher DTA peaks indicate purity of the analysed sample, in that there is more of the same substance being pyrolysed at its particular pyrolysis temperature. This presents an issue with potentially starch loaded biomass such as the Date Pit Core, as starch has a generally similar degradation peak range to cellulose and other glucose chains. The presence of starch can be confirmed by performing an iodine test for starch and observing a positive result. However, a clearer image that allows the interpretation of this peak as cellulose is presented in the DTA comparison between α-cellulose, Date Pit Core and Date Pit Whole (Figure 4.6), where there are small but obvious peaks at 150 – 250 °C and an enlarged peak that is in the favoured cellulose range such as the α-cellulose peak between 250 – 350 °C.

On this note, the size of the hemicellulose peak in Date Pit Core in comparison to Date Pit Whole is barely visible in the circled area. Coupled with the compared mass loss in the cellulose range, this would encourage the hypothesis that, as per seed biology, the DPC is densely packed with cellulose or starch, providing stocks of energy for seed embryo growth with little need for structural integrity as per the function of hemicellulose and lignin. Although this would show that the Date Pit Core should have less energy than Date Pit Skin, as lignin is found to have higher Gross Calorific Value than cellulose (Fuwape, 1989), the quantity of cellulose found in Date Pit Core would lead to overall higher energy content. It can also be seen from Table 4.1, that the Date Pit Skin has a higher fixed carbon content than the other two samples and according to research has a higher energy content as will be explored in section 4.1.2 (Demirbaş, 1997; Demirbaş, 2001; Pang et al., 2014; Saldrriaga et al., 2015). The large dip in the curves seen in Figure 4.6 is attributed to a polymer they all share in common, cellulose. Whereas the points where the curves end reveal the relative amounts of fixed carbon, showing the amount of unreactive carbon that contributes the most to the energy content of the biomass sample as carbon. This is made more visually clear in Figure 4.7 using the averages from multiple runs.

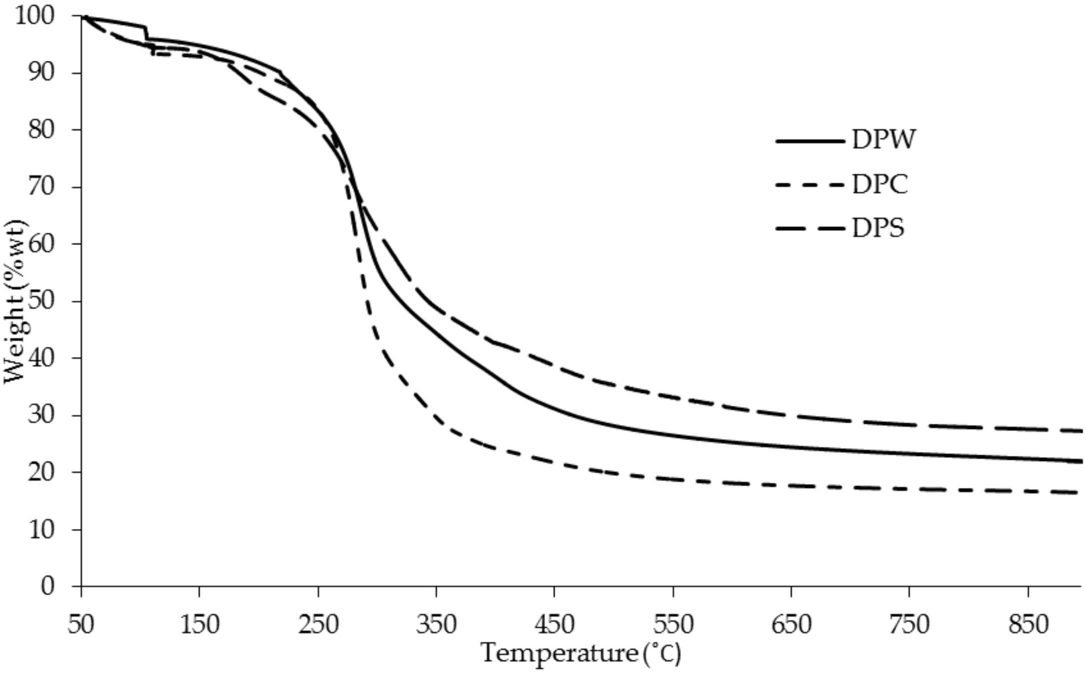

Figure 4.6 TGA of Date Pit Whole and its separated components, DP Core and DP Skin.

This information is relevant to future research as there is no data on DPC or DPS for any variety. With this knowledge, future research can be conducted on the examination or separation of these two components in bulk.

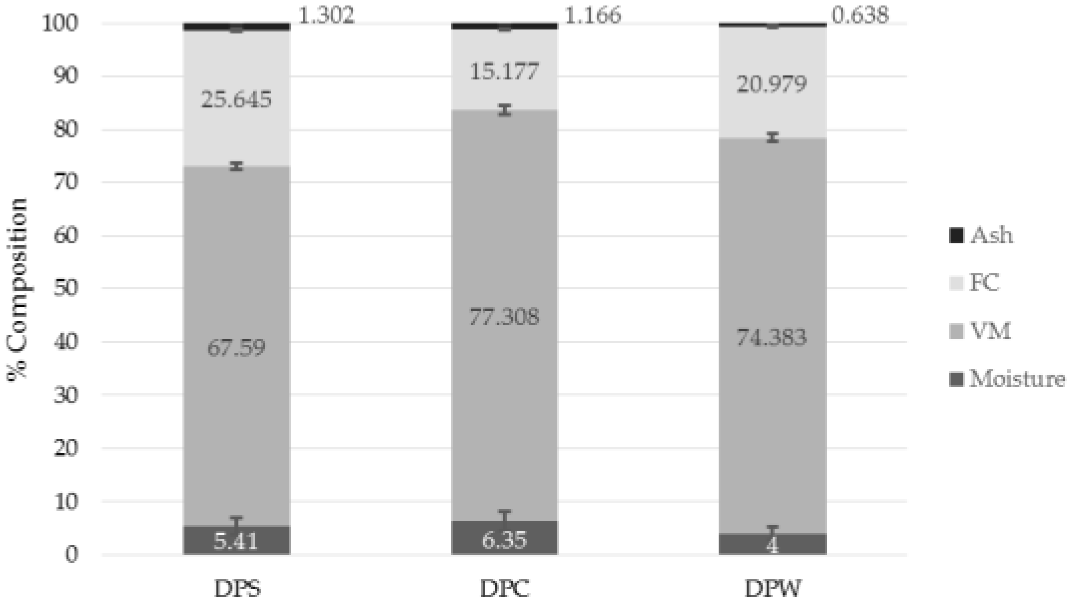

Figure 4.7 Visualisation of proximate analysis of Date Pit Skin, Date Pit Core and Date Pit Whole. The analysis was done in triplicate.

The ultimate analysis data obtained can be used for several purposes:

- Estimating the Gross Calorific Value/Higher Heating Value (GCV/HHV).
- Examination of clean burning capabilities (production of H_2O vs. NO_x).
- Comparison to other solid fuels and biomass.

In reference to the ultimate analysis results when compared to the proximate analysis, a relationship can be drawn between the data sets, such as the inference for higher energy content and efficiency (calculated by dividing the hydrogen content by the carbon content over 12). As it is shown in the fixed carbon content of Date Pit Skin via proximate analysis, the carbon content is relatively higher in the Skin than in the Date Pit Core. Inference that Skin would combust with a higher GCV than Core can also be drawn from the comparison of H/C mass to molar ratios in relation to nitrogen content. Although H/C ratio for Skin is calculated as lower than Core (1.59 and 1.95 respectively), the nitrogen content of Core is expected to significantly decrease the energy output in comparison to Skin (1.12 and 0.80 respectively, as seen in Table 4.1). It is also expected that a higher concentration of nitrogen would lead to higher production of NO_x, further reducing the potential energy obtained from combustion and essentially producing undesirable by-products in the volatile matter fraction. The energy contents of the studied fractions will be further explored in 4.1.2.

Other commonly used biomass feedstocks were also analysed in this way, providing a visual comparison between the potential biomass resources from a thermal standpoint. These feedstocks are compared to Date Pit Whole, to represent the differences in thermal characteristics between common feedstocks and a potential feedstock. The samples included oat husk, rapeseed and brewers spent grain (BSG), the TGA curves of which can be observed in Figure 4.8 and were compared to Date Pit Whole as standard biomass feedstocks. Several observations can be made from this collection of thermograms. The moisture content is lower in the date pits than the other biomass, meaning the date pits are inherently drier and potentially easier to pyrolyse since the total water content will take up less energy to boil out of the internal structure (this makes sense as date pits come from drier climates and have adapted as such). This also means water should theoretically not play such a significant role during dry microwave pyrolysis. The date pits also seem to closely follow the trend of BSG until > 450 °C, where the fixed carbon content is evidently higher in the rapeseed than date pits, suggesting that rapeseed has a higher energy content than date pits which is higher than the other biomass sources. The steep drop in mass for BSG and oat husk also reveal lower volatiles content and higher thermal stability in the date pits in comparison.

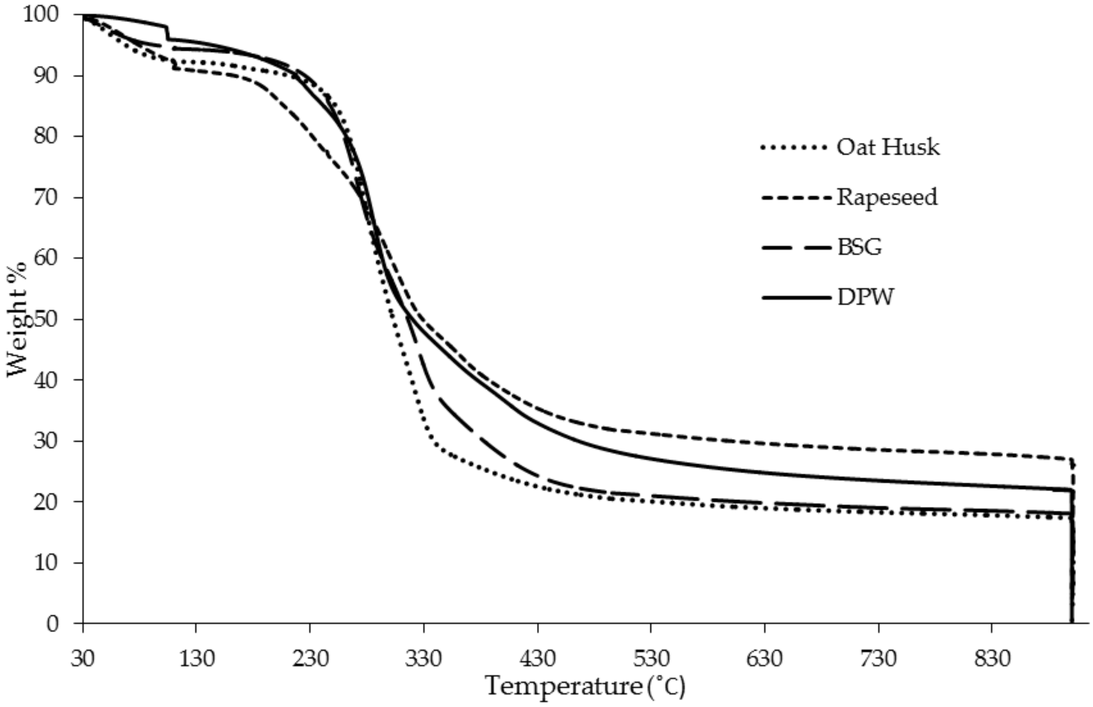

Figure 4.8 The TGA curves of common biomass feedstocks versus date pits.

4.1.2. Higher Heating Values

Traditionally, the higher heating value (HHV) or gross calorific value (GCV) of a material is obtained by using DSC or other forms of Calorimetry. However, due to time and equipment constraints for this study the researcher will be using estimates as obtaining the exact values is not necessary for the scope of this research. These estimation methods can also be used to quickly assess the changes that occur in the solid biomass yields of the chosen processes, while simultaneously gathering thermal analysis data to compare with other biomass and solid/liquid fuel sources. The equations used for estimation are listed below:

$HHV\ (in\ MJ/kg) = 0.196(FC) + 14.119$ **Equation 4.1** (Demirbaş, 1997)

$HHV\ (in\ MJ/kg) = 19.914 - 0.2324(Ash)$ **Equation 4.2** (Sheng & Azevedo, 2005)

$HHV\ (in\ MJ/kg) = -1.3675 + 0.3137(C) + 0.7009(H) + 0.0318(O)$ **Equation 4.3** (Sheng & Azevedo, 2005)

$HHV\ (in\ MJ/kg) = 0.1905(VM) + 0.2051(FC)$ **Equation 4.4** $(\mathrm{Yin}, 2011)$

Table 4.2 shows the results of Equation 4.1 to Equation 4.4, comparing them to raw data and literature values.

Table 4.2 A collection of solutions for the specified sample types. The estimated energy values are in MJ/kg. The solutions for the referenced materials were calculated based on proximate analysis data presented in the studies, in order to compare to the reported experimental values.

Type	Equation 4.1	Equation 4.2	Equation 4.3	Equation 4.4	Experimental	Reference
DPW	18.40	19.75	20.12	20.26	18.226 – 18.548	(Babiker et al., 2013)
DPC	17.19	19.63	19.66	19.89	---	This study
DPS	19.38	19.59	19.80	20.44	---	This study
α-cellulose	15.59	19.73	---	19.36	17.030	(Murphey & Masters, 1978)

The FC, VM and Ash values were all obtained from the proximate analysis of the respective samples. The C, H, N and O values were obtained from the ultimate analysis of the respective samples. (Note: The literature may be using date pits of a different variety and may show some variation). Table 4.2 shows the obtained results for the energy analysis of the date pit components and compares them to literature values obtained from reference studies. The results were calculated using the equations presented above and are intended to be used as estimations of the higher heating values obtainable from the biomass sources. They can also be used to observe the changes in energy, lignin and fixed carbon contents between the raw and processed date pits and across the processing conditions.

It is important to observe the closeness of the DPW estimate for Equation 4.1 to the referenced data. The value obtained also closely matched the final result of solving Dulong's formula (see Equation 4.5) for theoretical calculation of calorific value of a fuel. Since Babiker et al. used several popular varieties and obtained their respective HHV, a range is obtained where it can be expected that the researched biomass should have HHV values falling within this range (Babiker et al., 2013). Equation 4.1 uses the average FC of DPW and lies in this range, thus it can be assumed that this equation is useful for watching the changes in energy content of the date pit biomass before and after processing. This is also encouraged by the result of α – cellulose estimation, which is also relatively closer to the reported values in Equation 4.1 than in Equation 4.2 and Equation 4.4. It is also important to note that there are no reported values for the DPS and DPC, as this is a unique perspective for this thesis to physically separate the skin and the core of the date pits. This is likely due to most studies grinding date pits into powder instead of separating them for analytical purposes. This is good for this thesis as new information is presented on date pit biomass, where it can be seen that as the skin has more carbon and fixed carbon content, it is inferred to have higher energy content than the core. This is despite that the skin only accounts for about 15% of the date pits mass.

$$\frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240S\right]$$

Equation 4.5

This leads on to why these equations function in their respective literature and in this context. Since carbon content contributes to the energy content of the biomass, Equation 4.1 focuses on using the fixed carbon content as the primary factor in HHV estimation, with the constant being calculated in the literature after studying more than 10 different biomass feedstocks (Demirbaş, 1997). Carbon is expected to have a positive effect on the energy released during combustion of biomass, whereas oxygen would have a relatively negative and heat absorbing effect and would inherently reduce the energy content. Hydrogen would also contribute to increase the energy content of biomass; however it should be noted that hydrogen has a significantly lower presence in most biomass unless it is present as moisture which would reduce the energy content as it absorbs energy to evaporate. This would lead to a reduction in the overall mass, while not offering anything beneficial to the exothermic heat produced. Since lignin is a biopolymer made up of aromatic rings and thus ensuring relatively high carbon content, it can be expected to significantly contribute to the energy content of lignocellulosics biomass. This is evident in literature, as lignin (21 MJ/kg) has a significantly higher HHV than cellulose (17 MJ/kg) and despite being high energy sugar polymer (Murphey & Masters, 1978).

This then leads on to another expectation that the DPS would thus have higher lignin content than the DPC, evidenced by the proximate results (Refer to Table 4.1) showing a higher FC which is correlated to the lignin content as well as the energy estimates for the respective components (Table 4.2). This builds upon the hypothesis presented in 4.1.1 that suggested based on just the carbon contents and the colour of the components that there is more lignin in the skin than in the core and that the core is densely packed cellulose/starch. Purifying the lignin and cellulose components of the biomass might also suggest a pathway to enriching the energy content of the DPS and DPC respectively, while also providing evidence that separating the skin and core from each other without mechanical processing would be beneficial to obtain exclusive phenolic and sugar-rich yields.

While the estimation of energy content may not necessarily be accurate, this method can more easily build a profile with which the raw material and processed yields can be compared reliably, especially in cases where equipment or chemicals are unavailable or have restricted usage. Going forward, Equation 4.1 will be used to estimate the energy content of the processed yields as well as to develop an understanding of the HHV changes in comparison to the raw date pit biomass.

4.1.3. Lignin Content

One of this thesis's main challenges was finding reliable lignin quantification methods, and each came with its own challenges and benefits. The lignin content for this biomass sample was obtained using two different methods, the ABSL method and the TGA

Estimation method. The reason for this is not only to compare the approaches to each other but also to obtain a standardised answer to the question, "How much lignin can be extracted from a date pit?" Also, the researcher could not continue using the ABSL method due to unforeseen circumstances. Thus, a new, simpler, safer and more accessible way must be used and developed, and the TGA Estimation method was selected for this. Also, for the sake of consistency as Hatfield & Fukushima (2005) noted, this study will use this method to analyse the biomass before and after processing. This methodology will help determine whether or not there is a substantial quantitative change in the lignin content or at least an overall physiochemical change

The calibration of the standard curve was performed and recorded in Table 4.3. Using the calibration data, the extinction coefficients were plotted versus the absorbance and lignin concentration (Figure 4.9 and Figure 4.10 respectively). The trend line equations were then used to solve for the unknown concentrations of lignin in the date pit samples. The raw date pit lignin content estimates will be compared to the ABSL values, where the ABSL values are used as the accepted values and allowing selection of the more accurate set of equations. The results of the ABSL measurements can be found in Table 4.4.

Table 4.3 The measured lignin standards with their recorded absorbance. The respective extinction coefficients were calculated using the absorbance over the concentrations.

Lignin Standard (mg/10 mL)	Absorbance	Lignin Concentration. (μg/mL)	Extinction Coefficient.
0.4	0.876	400	0.00219
0.6	1.249	600	0.00208
0.8	1.490	800	0.00186
1.0	1.700	1000	0.0017
1.2	1.763	1200	0.00146

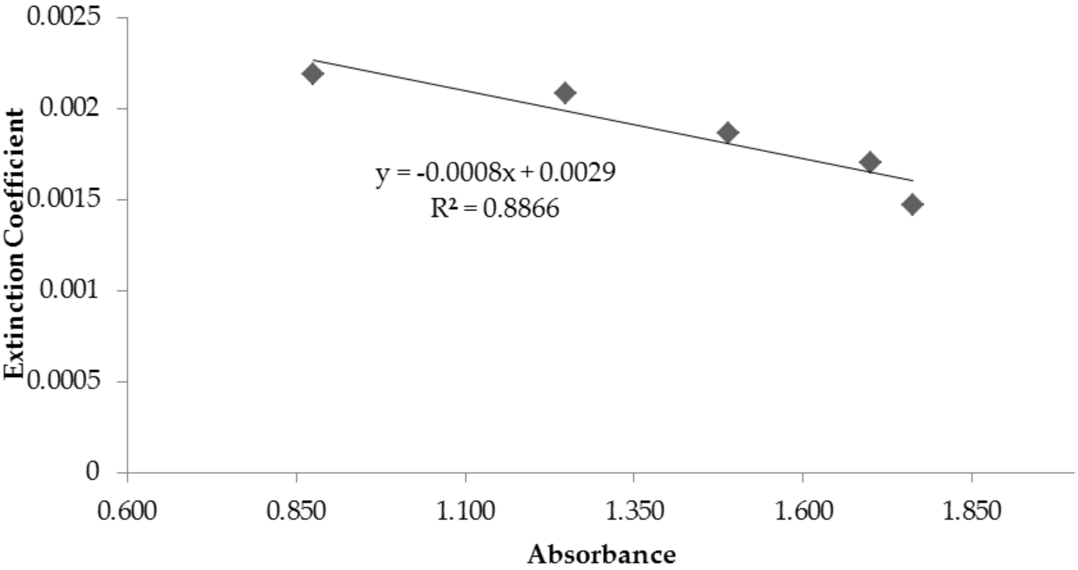

Figure 4.9 The calculated extinction coefficients versus the absorbance to determine the extinction coefficient of the tested samples.

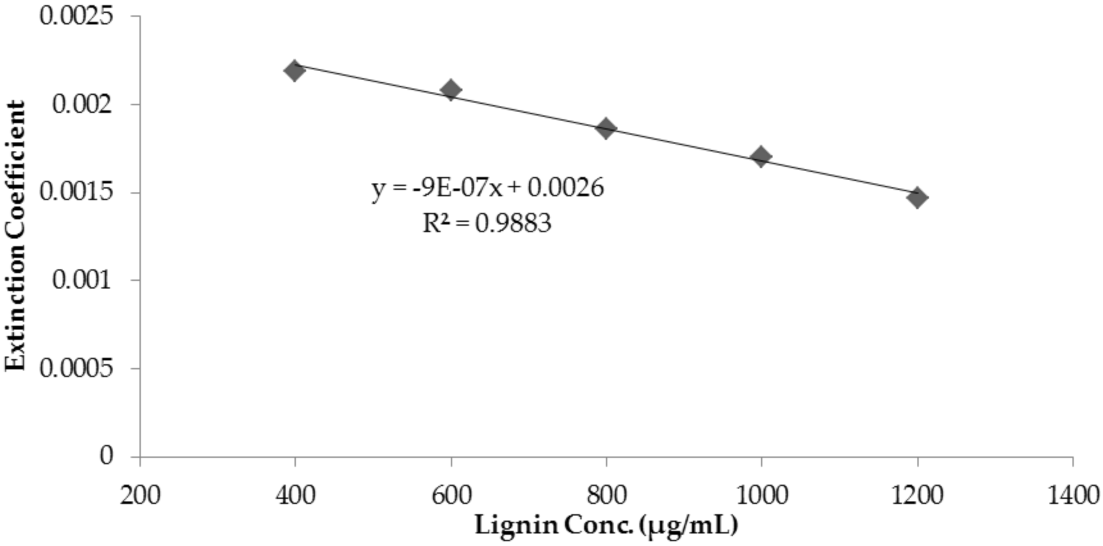

Figure 4.10 A chart showing the calculated extinction coefficient versus the lignin concentration (µg).

After obtaining the above trend line equations above (refer to Figure 4.9 and Figure 4.10), they were used to calculate the extinction coefficients and lignin concentrations respectively in the date pit skin and core samples as seen in Table 4.4.

Table 4.4 The calculated lignin content in the biomass samples based on the obtained absorbance and extinction coefficients.

Sample ID	Absorbance	Calculated Extinction Coefficient	Conc. (μg/mL)	Conc. (mg/mL)	Mass present in biomass (mg/100 mg)[1]
DPC 1	0.239	0.00271	120.89	0.121	3.87
DPC 2	0.197	0.00274	158.22	0.158	5.06
DPS 1	1.290	0.00187	813.33	0.813	26.03
DPS 2	1.426	0.00176	934.22	0.934	29.90

Using proximate analysis and TGA data obtained in 4.1.1 and 4.1.2, equations for lignin content[2] estimation based on HHV were used and can be found below (see Equation 4.6 and Equation 4.7). These equations were originally meant to quantify the HHV of biomass samples using the lignin content as a variable, and were used to calculate the lignin content within reasonable expectations using the estimated HHV. It should be noted that the input values for FC should be on a dry, ash free basis. The solutions of the lignin estimation equations were recorded in

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[1] Dry, ash free and extractives free basis.

[2] Lignin content is reported as a dry, ash free and extractives free basis.

Table 4.5. To simplify the output of the lignin estimation results, the solutions for Equation 4.1 were used as an input variable for the respective samples, to be compared to the ABSL values.

$HHV\ (in\ MJ/kg) = 0.0864(LC) + 16.6922$ **Equation 4.6** (Demirbaş, 2003)

$HHV\ (in\ MJ/kg) = 0.0979(LC) + 16.292$ **Equation 4.7** (Acar & Ayanoglu, 2012)

Table 4.5 A comparison of lignin values determined by different methods; comparing HHV/lignin estimates to the ABSL experimental data.

Sample ID	Equation 4.6[1]	Equation 4.7[1]	ABSL[1]	Reported	Reference
DPC	5.7	10.3	4.47[2]	---	
DPS	31.1	31.5	27.96[2]	---	
DPW	19.8	21.5	---	37.03[3]	(Nasser et al., 2016)

The data in Table 4.5 is meant to show the closeness of the data points and validity of using a TGA methodology for estimating lignin content (which can provide proximate analysis data simultaneously) in comparison to ABSL data.

Based on the estimations provided by these equations, several points have been observed:

1. They have good comparison and closeness to ABSL values, with the variations explained by the natural variability of biomass and other minor contributors to the fixed carbon content. However, Equation 4.6 is significantly closer to the ABSL value than Equation 4.7. This closeness is likely due to the author of Equation 4.6 testing more samples and establishing a stronger relationship between fixed carbon (FC) content, higher heating values (HHV) and lignin content (LC) of the biomass samples. It is vital to note that both Demirbaş and Acar & Ayanoglu did not use the ABSL methodology to determine the lignin contents of their representatives (Acar & Ayanoglu, 2012; Demirbaş, 2003).
2. As long as consistency is maintained, thermo-gravimetric analysis and data can remain an acceptable indicator of phenolic content change in the biomass as well as useful under circumstances that would inhibit lab or equipment access for this thesis.

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[1] Dry, ash free and extractives free basis.
[2] Mean results.
[3] Lignin content is reported as a dry, ash free and extractives free basis.

3. The equations show more inconsistency with ABSL when analysing samples with lower fixed carbon content but are still able to detect significant differences in lignin content between the core and skin of the date pits.

4.1.4. Point Load / Strength Test

Due to the unique shape of date pits, the analysis had to be conducted on two axes or orientations: focusing the point force between the furrow and seed (relatively low thickness) or on the sides (maximum thickness), the results of which are presented in Table 4.6. It can be observed that the values range between 1.5 – 2.0 kN meaning it would take on average 3 – 4 adults standing on top of one pit, under Earth's gravity to crush it. A point to consider is that while the "side" values were consistent, the "groove" values were slightly dependant on the relative size of the date pit and shape of the furrow (closed or open, thus making a thinner point of measurement and dividing the date pit). Despite this, it is evident that at the thickest points the date pits withstand up to 2.0 kN of force. It can be anticipated that the average force to crush a whole date pit is roughly 1.5 kN.

Table 4.6 Point load test results on the raw date pit.

Orientation	Point Load Values (kN)			Average
	1	2	3	
Side	2.0	2.0	2.0	2.0
Groove	0.5	1.5	1.0	1.0 ± 0.4

This information is crucial as it indicates the tensile strength and initial impact force required to break date pits into fragments and powder. Of course, as they fragment, they will likely need more energy and time to produce a uniform powder, but this measurement can indicate how much softer the date pits become after processing.

4.1.5. Dielectric Analysis

While grinding is a useful method to prepare the date pit biomass for pre-treatment and extraction, it has been determined so far that the majority of phenolics and sugars are inherently separated into 2 layers of skin and core. This leads to a prospect that the raw date pits can be at least prepared by separating these layers without mechanical processing. Due to this as well as the nature of the analysis method, a whole raw date pit could not be analysed and has been split into 2 sections for analyses. For this research thesis, microwave processing was proposed and thus required dielectric analysis of the raw materials in order to understand the expected microwave heating behaviour of the different parts of the date pits.

The dielectric constant (**ε’**) and loss, (**ε’’**) of the core and skin samples were measured versus temperature, and were plotted to observe trending changes (See Figure 4.11 for DPC and Figure 4.12 for DPS).

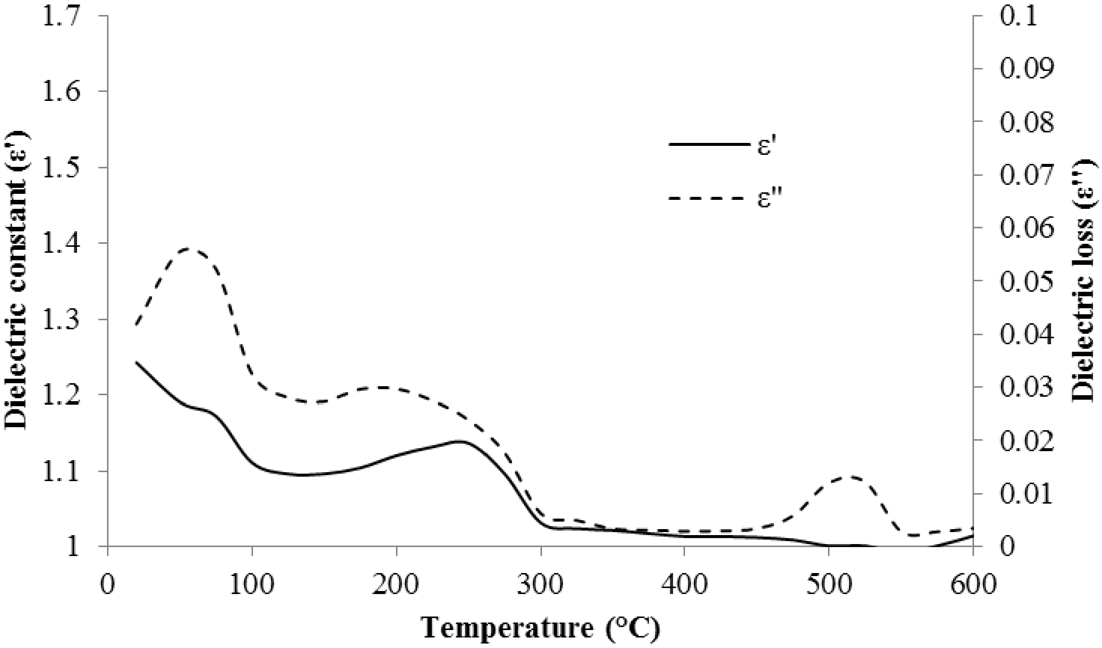

Figure 4.11 Dielectric properties of the DPC sample, measured at 2.45 GHz.

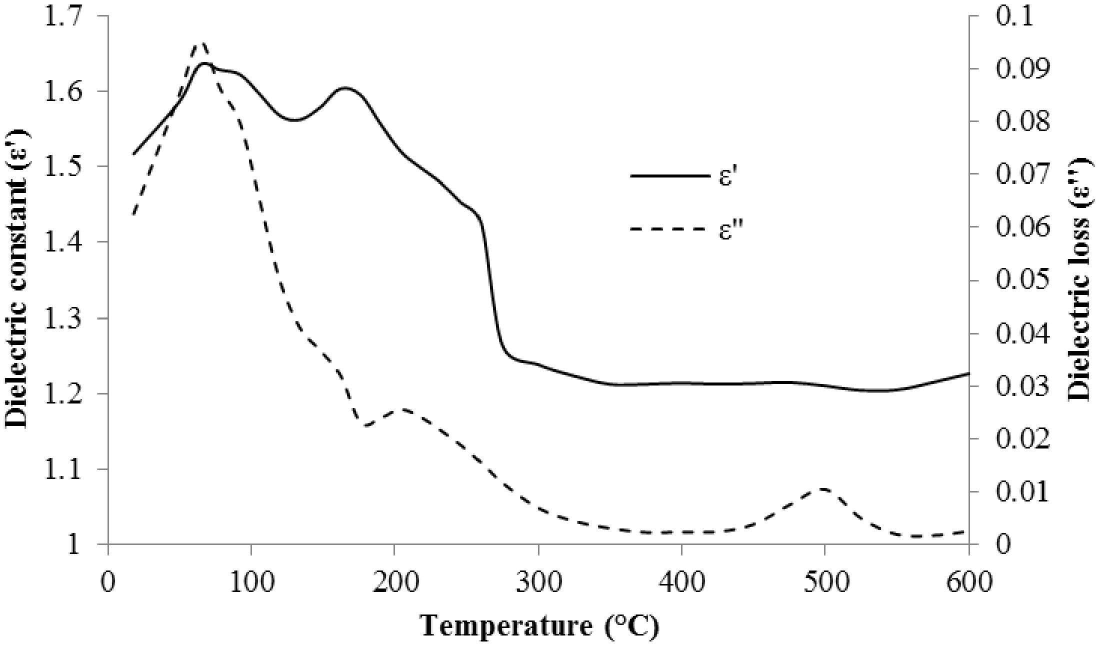

Figure 4.12 Dielectric properties of the DPS sample, measured at 2.45 GHz.

While the dielectric values remain relatively low for biomass and dry materials, the main objective of this analysis is to observe trends and understand what is causing them, in the hopes that they can be exploited to maximise the process method and yields. This is also based on the fact that the volatiles escape as they are pyrolysed, so the measurements are based on analysing residual volatiles. Since most changes can be observed occurring < 300 °C for both samples, this makes it easier based on the previous analyses to determine what is occurring at each peak. Peaks in this range are an indication that moisture evaporation and hemicellulose degradation contribute the most to spiking dielectric properties of biomass that does not normally absorb microwaves well. It can be observed from Figure 4.11 that as temperature rises towards the water boiling point, a significant rise and drop in ε'' occurs up to 100 °C in the DPC sample. This is even more apparent in the DPS sample (Figure 4.12), where both ε' and ε'' rise and dip at a similar pace, as opposed to DPC ε' that has a minor plateau but overall continues decreasing. All of this can be attributed to water evaporating within the date pit cells and minor extractives evolving. The interesting aspects occur between 150 - 250 °C, where both samples exhibit an increase in both properties. While DPS has a short period of increase before steadily declining, DPC maintains this rise until 250 °C where both ε' and ε'' sharply decrease. This region as stated previously should be attributed to the degradation of hemicellulose and the subsequent formation of products such as furfural and furans, which are some of the main degradation products of hemicellulose and cellulose. It should be noted that furfural has significantly higher values for ε' and ε'' than cellulose below 200 °C (Furfural at 150 °C: ε' = 22.818, ε''= 2.797; Cellulose at 150 °C: ε' = 1.798, ε''= 0.122.). This would encourage selective heating to prioritise the thermal products of hemicellulose. Both samples also reveal a slight peak around 500 °C, though this peak can be attributed solely to lignin degradation and formation of phenolic products.

Due to significant changes in the dielectric properties and composition occurring below 300 °C in Figure 4.12, another analysis was performed primarily on the DPS sample as it is expected to have a more complex and diverse composition than DPC, focusing on this region with smaller gaps between data points. It can be seen clearly that the peaks that appeared < 200 °C in Figure 4.12 are slightly more defined, with shoulders appearing between 80 – 100 °C for ε' and ε''. The shoulder in ε'' at ~160 °C is also interesting as it could be attributed to the formation of hemicellulose pyrolysates. Since it is difficult to pressurise and contain these pyrolysates, it would thus be a difficult point to verify without further and alternative analysis.

The above figures show that there is significant dielectric activity between 50 – 100 °C and 150 – 200 °C. This can be deduced as representing the evaporation and movement of water molecules and the breakdown of hemicellulose within the biomass infrastructure respectively, as the temperature ranges correlate with the analytical data in 4.1.1 (see Figure 4.13 below).

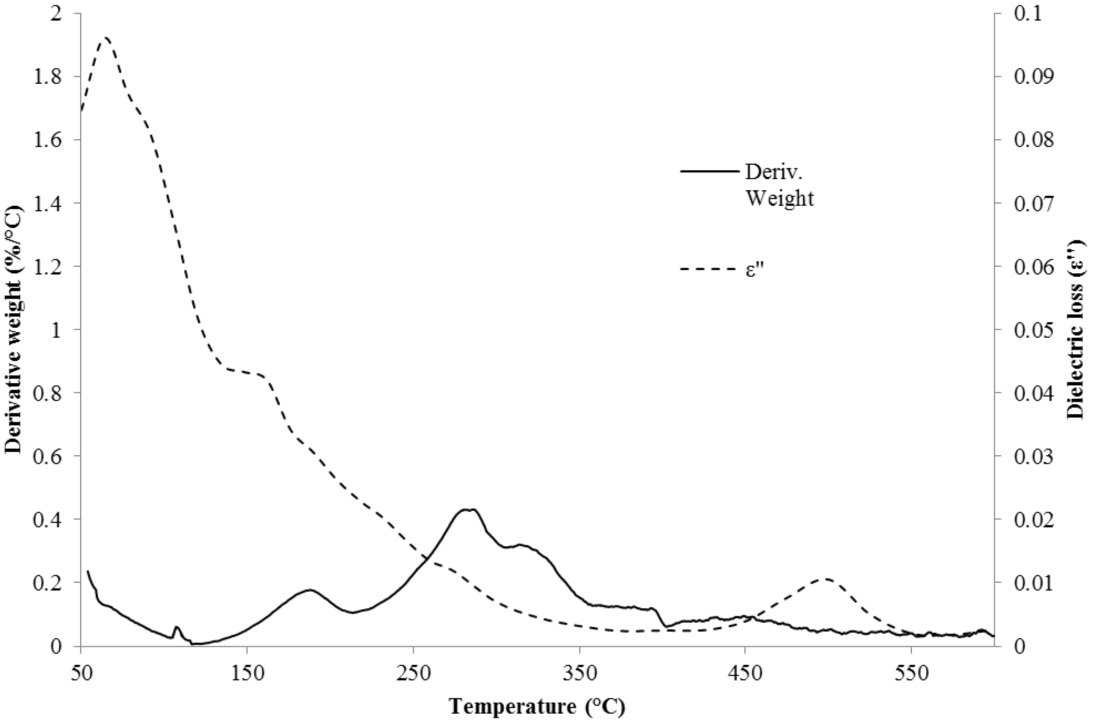

Figure 4.13 Dielectric loss and DTA of DPS from 50 – 600 °C.

This visualisation reveals two key temperature stages below 300 °C which can be exploited in microwave processing: water evaporation and hemicellulose degradation. Selective heating would occur in this scenario/sample when the dielectric loss for specific materials are higher than neighboring substances, in this case water would be selectively heated until reaching a point under pressure where it is no longer favoured by microwaves (refer to Table 5.7). The heating of water trapped in cells and structures can in theory induce a small-scale subcritical state, breaking down hemicellulose faster and inducing selective heating at higher temperatures due to furfural and other by-products. Thereby providing a focal point for the microwaves and pyrolysing the date pits more effectively and rapidly by adding more lossy and inducing further selective heating during the breakdown of hemicellulose. As seen below, furfural would have a higher dielectric loss value than water before it reaches a subcritical state. This chain of events can lead to higher internal temperatures within the date pit core (which has fewer microwave transparent and thermally stable phenolic components than the skin). The higher internal temperatures will lead to hotter controlled pyrolysis conditions, thus removing undesirable components and ensuring generation of carbonised yields and potential bio-oil vapours.

Table 4.7 Reference data for materials measured at 2.45 GHz

Material	Dielectric Loss ε’’	References
Water (20 °C)	~14.5	(Komarov & Tang, 2004)
Water (100 °C)	~1.8	(Komarov & Tang, 2004)
Furfural (100 °C)	4.606	(Robinson et al., 2021)
Furfural (150 °C)	2.797	(Robinson et al., 2021)

4.1.6. Py-GC/MS Analysis

The results of the Py-GC/MS are outlined below. The main focus here is to use this information to indirectly obtain lignin content as well as information on other potential sugar based yields. The table of grouped components found in the retrieved chromatographs for DPS and DPC are shown below in Table 4.8. The pyro-chromatographs and the peak identification tables for DPS and DPC can be found in Appendix C.

For this purpose, short chained and cyclic non-aromatic components were attributed to a sugar fraction, whereas aromatic and phenolic components were equated to lignin content. Long chained acid were grouped as fatty acids. It is not clear if some of the sugar – based derivatives belong to cellulose or hemicellulose using this method, adding to the effort of solving for the cellulose content specifically but these can be combined to form a holocellulose section, which is essentially total polysaccharides/sugars present in plant samples. Melezitose, shown below in Figure 4.14 (an example of a pyrolysate which is present in both samples) is essentially 2 glucose units connected by a furan and thus may be attributed to either cellulose or hemicellulose.

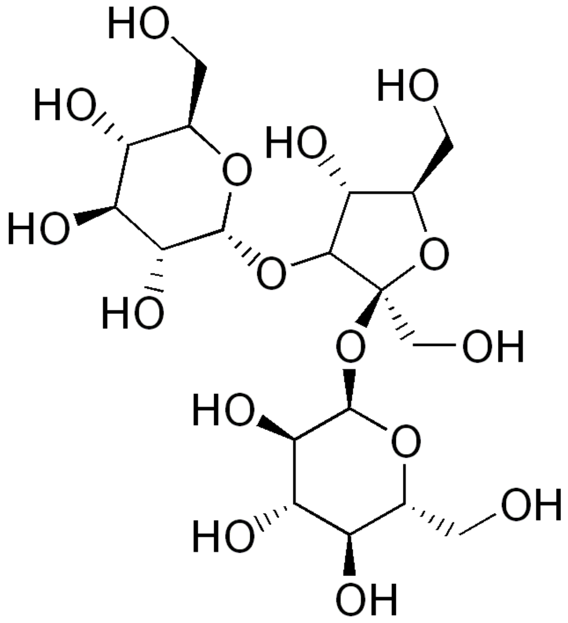

Figure 4.14 Melezitose, 2 glucose units connected by a furan/xylose, and it can found in both DPS and DPC pyrograms.

Several assumptions were made based on literature (the degradation pathways of the lignocellulosic components), and TGA data obtained in this study (the thermal stability of hemicellulose, cellulose and lignin chains). The TGA analysis specifically shows that the first peak corresponding to hemicellulose degradation occurs between 150 – 250 °C, while cellulose degrades at a significantly higher rate above 300 °C. Based on recent studies, it can be assumed that most furanic compounds are related to hemicellulose degradation (Delbecq et al., 2018; Luo et al., 2019). Pyranoses and some furans can be attributed to cellulose pyrolysis and dehydration. Furans can also be generated from further degradation of cellulose by-products. There is also a chance that most of the hydrocarbons are exposed to higher temperature pockets during pyrolysis, degrading into water and smaller hydrocarbons such as 1C and 2C products. Meanwhile, considering the comparatively high thermal stability of cellulose and lignin in DPS and DPC, it can be expected that 6C cyclic by-products belong to the cellulose or phenolic groups depending on the presence of oxygen within the ring/chain or benzene rings. The fatty acids are in a category of their own as they clearly do not come from the cellulose or lignin fractions of biomass.

By classifying the fragments and associating them to their parent component, a picture can be built of the composition of the analysed material as shown in Table 4.8. A comparison is made to other biomass, however the methodology used in the literature presented is focused mainly on the lignin/phenolic fraction of the biomass and as such filtered out the information on the undefined parts of the pyrograms (Ware, 2013). It can be assumed the remaining fractions belong to the sugar components that broke down further into CO_2 and water. The same can be said of Hidayat et al., but a more diverse spread of hydrocarbons can be seen in this study, especially furans which can theoretically be derived from cellulose though more likely than not had degraded into lighter compounds (2018). This leaves a large room for error using this method to analyse the date pit biomass considering that all lignocellulosic material can breakdown further into CO_2 and water, but based on the thermal stability of lignin and its products this is an unlikely source. As for cellulose and hemicellulose, while furfural and levoglucosan can break down further, the evidence of pyrans and furans show potential for most of them to remain intact at lower processing temperatures and thus lead to a usable amount of sugary bio-oil. This methodology also does not restrict the search for the sugar based pyrolysis products, despite being adapted from the referenced studies, so it is promising to see them in good quantities, especially from the core which contributes the most to a date pits mass.

Table 4.8 A compilation of the pyrolysates of DPS and DPC and their classification, with comparisons to previously studied leaves and grass.

Group Component	**% Composition from Pyrograms**			
	Skin (DPS)	**Core (DPC)**	**Wild-Type Sorghum Leaves** (Ware, 2013)	***Imperata cylindrical*** **(500 °C,** (Hidayat et al., 2018)**)**
Short-chained compounds (> 2C, ≤6C)	12.16	12.48	9.4	11.1
Furans (4C, 1O rings)	9.44	35.34	11.83	17.92
Glucose related compounds) / Pyranoses (5C, 1O rings)	13.09	29.71	0.93	---
Aromatics and 6C rings	51.09	4.07	28.51	65.61
- Catechol	**13.93**	**1.68**	**---**	**---**
Long Chained Organic/Fatty Acids (> 8C)	14.21	18.43	---	4.3

Undefined	---	---	49.33	1.07

To easily interpret this table, the following is a list of how major compounds and their analogues contribute to interpretation of pyrograms now and in the coming chapters:

- Short chain compounds such as butane, ethanol and acetic acid are grouped together and with consideration to flash pyrolysis are formed by all three lignocellulosic macromolecules. They will be considered as contributing to both the hemicellulose and cellulose fractions mainly due to the thermal stability of the lignin fraction seen in the TGA data (suggested by the fixed carbon contents of the samples).
- The “Furans” group consists mainly of 4C sugars and analogues such as furanose, furfural and 2-Furanmethanol. Butanes may also be considered as part of this group depending on their overall structure but unlikely. These compounds are mainly formed from sugars that make up hemicellulose, with a small percentage breaking down from cellulose pyrolysis.
- Pyranoses and glucose compounds are group based on them having an oxygen within a 5C ring and are primarily sourced from cellulose, with a potential few forming from incomplete pyrolysis of hemicellulose.
- Aromatics belong strictly to phenols found in lignin chains as there is almost no other source of benzene/phenolic rings in biomass. 6C rings are also a small part of this group as they can represent oxidised phenols.
- Long chained hydrocarbons and fatty acids fall into a category on their own and depending on the biomass source, can form a basis for the production of bio-diesel.

A key component that is present in both samples is catechol, which is a good indicator of lignin/phenolic quantities in lignocellulosic date pit biomass and its parts. As the quantity of catechol present in DPS is ~8 times the quantity found in DPC. This point is reflected in the TGA (~3.5 x) and ABSL (~6 x) estimations of lignin contents of the respective samples (Seen previously in Section 4.1.3). This compilation of data confirms that the vast majority of phenolics are present in the outer layers of the date pits, which are deemed microwave transparent at lower temperatures in comparison to hemicellulose and its derivatives. This increases the chances of the microwaves inducing fast pyrolysis conditions in the centre of the date pit biomass. This would be beneficial as this may uniformly breakdown the hemicellulose across the lignocellulosic structure and loosen the connection the skin has to the core, while also increases the chances of cellulose pyrolysis leading to several possible outcomes:

- Increased bio-oil yield with high energy, glucose based fermentable fractions.
- Breakdown of holocellulosic bonds, making extraction of high sugar yields possible without the interference of hemicellulose fractions.
- Simplifying lignin separation due to breakdown of hemicellulose linkages to cellulose.

The results from this section show for the first time, that the lignocellulosic material in date pits is inherently separated in 2 layers; a starch and sugar rich core and phenolic/lignin rich skin layer. Now would be the task of this thesis to develop a separation method for these materials, or to subvert the mechanical processing methodologies that would mean extracting the lignin from a less energy rich source.

4.2. Hydrothermal Microwave Results

The objective of this experimental stage is to extract lignin as a solid residue using an environmentally benign and energy efficient method. Due to subcritical water changing its polar properties with increasing temperatures, the expectation is that this process would treat the date pits with one solvent of varying polarities and high temperatures, to degrade the lignocellulosic (mainly hemicellulose) linkages and liberate the valuable lignin fraction. The analysis carried out in 4.1 has informed the aims of this section: to separate the 2 layers by pre-treating the date pits and releasing the lignin rich skin from the starchy core, allowing for further processing of both downstream. Previous approaches to process date pits have all involved grinding them as a uniform powdered feedstock. Results from section 4.1 indicate that by treating the date pits as a potential source of two separable feedstocks can be beneficial and as mentioned in Section 3.3.1, the processing conditions were set with consideration to safe use limits of the apparatus (maximum 180 °C, < 20 bar), it should also be noted that the temperature range was ideal for degrading hemicellulose without encroaching into the cellulose degradation range and leaving a majority of lignin intact in the date pits, thus protecting the energy rich and highly valuable fractions of the biomass. Also hypothetically, during the initial heating phase of the solvent, the microwaves would penetrate the water and interact directly with the biomass once the temperature had reached subcritical stages (>100 °C) (refer to 4.1.5). At subcritical temperatures (for water), the dielectric properties of furfural at 150 °C are: ε' = 22.818, ε''= 2.797, while cellulose at 150 °C: ε' = 1.798, ε''= 0.122, meaning that furfural (formed from hemicellulose pyrolysis) would have significant preference by microwave heating over cellulose. Subcritical water would also become microwave transparent (Herrero et al., 2013), in comparison to the water contained within the date pits or substances that have formed in the early stages of hydrothermal processing (e.g. furfural). To give more clarity as to the yields obtained from this method, Figure 4.15 presents a schematic showing the terminology used to describe the three product streams resulting from hydrothermal microwave treatment.

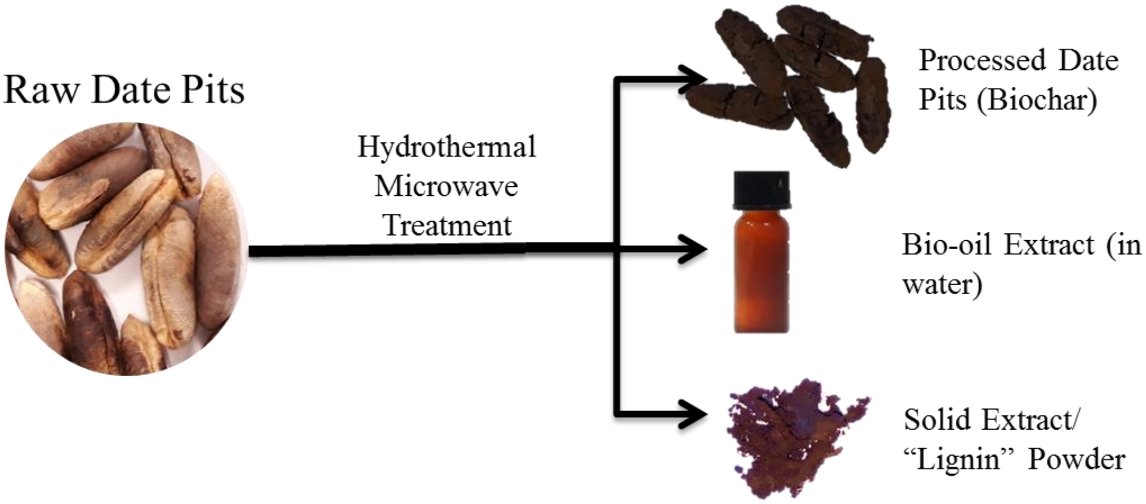

Figure 4.15 The yields obtained from hydrothermally processed date pits.

4.2.1. The Processed Date Pits

The changes to the date pits were observed based on their overall mass loss and collection of their residues for analyses to build a mass balance equation, with focus on lignin/phenolic extract yields. Table 4.9 shows the mass loss changes that occur to individual dates. The images of each respective run can be seen in Figure 4.16. Mass loss is a good indicator and comparison tool between the processing methods, as it can be easily tracked and can in itself provide evidence of lowered density (assuming the date pits maintained their volume) and retention/loss of water or lignocellulosic material.

Table 4.9 The mass loss results of hydrothermally processed date pits as a percentage of the initial mass under the experimental conditions. Statistical data was obtained from 180 °C, 30 minute runs done in triplicate. SD = 0.74%, Variance = 0.55%

Time (min)	**5**	**15**	**30**	**45**	**60**
Temp (°C)					
150	6.5	7.3	5.7	6.9	6.9
160	2.9	1.8	6.6	8.5	12.4
170	1.1	6.5	9.0	10.6	16.8
180	11.4	13.7	14.0	17.7	24.5

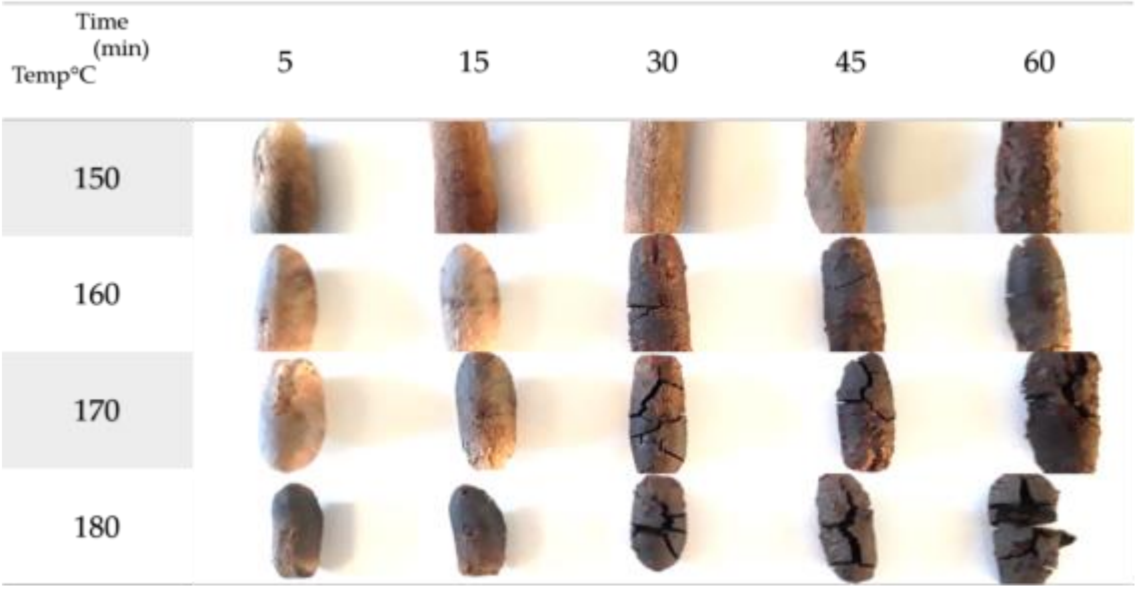

Figure 4.16 Images of the respective results tabulated above (Table 4.9) showing the physical effects of mass loss and hydrothermal pyrolysis. With little change occurring in the top left to significant softness changes in the bottom right.

One of the primary observations is seen at 150 °C, where the mass loss is similar and and generally ≤ 7% throughout the experiment times. Considering that the date pits were dried before raw analysis and prior/post processing, it would not be reaching to assume that this mass loss is attributed to free water lost during the drying process. This may also be related to degradation of some of the weaker bonds within the hemicellulose polymer, as this is entering the temperature range for hemicellulose degradation; however the compiled DTA chart of the processed date pits below (see Figure 4.18) shows a significant peak within that range. This is highly probable indication that there is still a notable amount of hemicellulose polymer present in the processed date pits at 150 °C.

At 160 °C, there is notable browning with increasing processing times, corresponding with increasing mass loss. It is clear that the temperature conditions are approaching the threshold to thermally degrade hemicellulose and light components from the date pit biomass, as is evidenced by the browning or caramelisation of the sugars in the biomass. It is at the 45 min trial that the hardness of the date pits drop to < 0.5 kN, showing that though the mass has not been reduced, the linkages maintaining the strong lignocellulosic structures have been severed enough to allow for mechanical processing.

For the 170 °C temperature conditions, the increasing mass loss over time trend remains and becomes more intense. The increase is such that the bonds have clearly weakened and is noticeable in the cracks and breakages observed in the images presented above. There is also significant browning and charring occurring by the 60 minutes trials, 16.8% of the date pits mass had been lost showing that a good amount of the lighter sugars had caramelised and pyrolysed. There was no “lignin” powder/extract that had been recovered but there was some bio-oil that was able to be tested in the Py-GC/MS analysis later.

A strange trend can be seen down the 5 minute time condition in that the mass loss decreases and then spikes at the 180 °C trial. It is likely that degradation of some of the extracts recalcitrate back onto the date pit up to 170 °C, then at 180 °C the pyrolysis products become more incapable of binding back onto the biomass, thus the increase in mass loss. When analysing the 180 °C temperature condition, the charring occurs very early as well as some structural failure at 15 minutes. By the 30 minute mark, the date pits start to resemble those from the 170 °C, 60 minute trial, with significant charring and breakage along the middle of the date pit. Not pictured and good to know is that the furrow on the underside had also closed up as a consequence of the extraction products and gasses escaping outward through the broken hemicellulose channels, leading to the breakdown seen in the 60 minute trial.

The maximum allowable amount was 7 date pits (~0.07 g/mL) with the minimum being 3 date pits (~0.03 g/mL) as more would be above water level in the experiment vessel. Table 4.10 presents the data of processing 7 date pits under maximum yield conditions (180 °C, 60 min), showing the mass loss and collected extracts and showing that despite the increased mass input, the solid extract had reached a similar yield output (0.3%).

Table 4.10 Extracts and yields obtained from hydrothermal processing at maximum experimental conditions, 7 date pits at 180 °C for 60 mins.

Mass In (g)	**Avg. Mass In (g/pit)**	**Mass Out (g)**	**Avg. Mass Out (g/pit)**	**Mass loss (%)**	**Liquid Yield (g)**	**“Lignin” Powder Yield (g)**
4.5911	0.6570	3.4012	0.4859	26.0	0.2919 (6.3%)	0.015 (0.3%)

A key observation is the fact that regardless of input mass between 0.03 – 0.07 g/mL, the mass loss percentage is similar at either end. This is an indication that this range is suitable for optimal processing. However the constraints of the vessel should be taken into account, as the shape of date pits and the curved bottom of the vessel limited close packing of the date pits and thus led to 7 being an acceptable maximum. There was also a notable drop in their density despite the date pits having and maintaining their volume post-processing (~700 mm^3). Their starting density was around 930 – 950 kg/m^3 and was reduced to around 680 – 700 kg/m^3. These values are comparable to the densities of hardwood and paper respectively, showing the vast change from hard to soft and the potential dramatic reduction of mechanical processing times to produce cellulosic (and somewhat caramelised) powder.

According to Gould et al., the lignin fraction can be separated from the internal lignocellulosic structure it is bonded to, but will more likely coalesce on the surface of the biomass during hydrothermal treatment (2016). This would explain the low solid extract yields (0.32 mg phenolic extract/ 100mg of date pits), under the assumption the “Solid Extract” is majority lignin powder, the expectation was that the date pits would incur up to 30% mass loss (removal of hemicellulose and some lignin) and this would be seen in the production of a more significant amount of lignin extract, with potential yields between 8 – 21 (mg /100 mg) based on the lignin content estimations (taking into account most of the lignin is in the skin, which accounts for 15% of the date pits mass). This is important data to obtain since it indicates that the hydrothermal microwave method is not useful for separating the phenolic fraction from the cellulose fraction due to the low yield of lignin rich phenolic extract. The mass loss and structural failure does confirm that the low energy sugars and hemicellulose linkages were indeed broken and allowing for the reddish brown substance to separate from the date pit as shown in the research by Gould et al. other intermolecular mechanisms would have contributed to the recalcitrance of the lignin fraction back onto the date pits. An advantage to this occurring is that washing the date pits post processing can dislodge more particles with ethanol or weaker acids while preserving their polymeric chain size and composition. SEM imagery can show globules of what Gould et al. expect to be lignin forming within 15 minutes of processing (see Figure 4.17). While the quantity itself is low, its value has shown a significant increase such that: at the cheapest rate of £470 per ton of lignin, using 7p worth of dates, about £10 – 20 worth of lignin powder was obtained (depending on the purity of the powder, which will be examined in the next section).

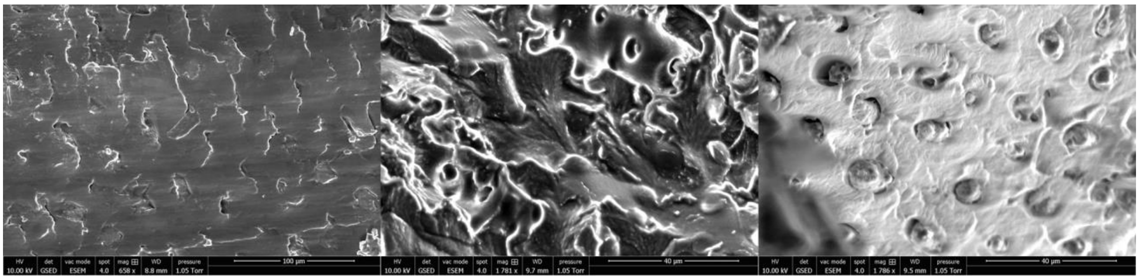

Figure 4.17 SEM imagery of the date pit core, from left to right: unprocessed, processed at 180 °C for 1 minute and processed at 180 °C for 15 minutes. The pores form within a minute and lignin globules form in less than 15 minutes.

The liquid yield is the bio-oil that was separated and dried from processing water, likely to contain most of the degradation products of hemicellulose dissolved in it and a small non-aqueous layer observed thus solidifying the presence of an oil fraction. The colour of the solution is due to caramelisation or the Maillard (Chichester et al., 1986; Maillard, 1912) reaction of the sugars in the date pit, occurring to both the hemicellulose pyrolysis products and the cellulose glucose monomers.

The alternative benefit of this method is that it manages to succeed at lowering the overall mass while maintaining the overall volume/structure of the date pits and their valuable lignocellulosic content to a great extent. This is preserving their sugar and phenolic content and lowering their density, in turn lowering their transportation/mechanical processing costs, increasing their potential value as a platform chemical or energy source.

Proximate analysis of the processed date pits was conducted and the 60 minute samples for the temperature range of 150 – 180 °C are presented below (see Table 4.11), while the results of all experiments are presented in the appendices and in detail, showing the trends based on time (A).

Table 4.11 Proximate analysis, energy and lignin content estimations of the processed date pits in comparison to the raw date pit.

Sample ID	**VM**[1]	**FC**[1]	**Ash**[1]	**Mois.**	**HHV (MJ/kg)**	**Estimated Lignin (%)**[2]	**Point Strength (kN)**	**Mass Loss (%)**
DPW	77.45	21.84	0.71	4.09	18.40	19.8	1.5	---
150C, 60min	73.31	25.68	1.01	2.23	19.15	28.4	0.5	6.9
160C, 60min	72.58	26.40	1.03	3.25	19.29	30.1	<0.5	12.4
170C, 60min	72.95	26.02	1.02	3.28	19.22	29.3	<0.5	16.8
180C, 60min	73.36	25.62	1.02	2.25	19.14	28.3	<0.5	24.5

One of the key points is the rise in fixed carbon content across all trials in comparison to the raw date pit (DPW), showing the degree of carbonisation that occurred due to hydrothermal processing. This could also indicate an increased concentration of components that cannot volatise easily such as high weight biopolymers, cellulose and lignins in this case. As discussed in Sections 2.4.3 and 4.1, the change in fixed carbon content can directly affect energy and lignin contents in biomass. This is made evident by observing the general increase in the energy and lignin content estimations in Table 4.11, although the slight decrease in respective contents as temperatures are increased should be noted as well. The increased lignin concentration in all the samples at 60 minutes is evidence that the lower energy components had been removed, but the

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[1] Dry weight % basis

[2] Dry, ash free and extractives free basis.

low solid extract yields for 170 and 180 °C helps to understand that the lignin that was expected to be removed has inherently been enriched within the date pit residue. This result is in agreement with findings of Fang et al. where lignin content in date palm biomass (leaflets and rachis) had significantly increased, as well as the content of sugar based biopolymers except for xylan (the main biopolymer that makes up most of hemicellulose) which had considerably decreased (2015). Another minor detail is the uniform drop and similarity in moisture content, presenting a case that the date pits are drier as a result of the hydrothermal process or are less able to retain water during drying.

Another trend to observe is that as the mass loss increases with increasing temperature, the energy and lignin contents remain roughly the same throughout. This finding is promising because it works with the narrative that the grinding costs and times would decrease due to lowered densities. Lowering pre-processing costs can increase the value of date pits as a potential fuel and platform chemicals source since it is now easier to obtain the higher value biopolymers such as cellulose and lignin. This is evidenced by the significant drop in point load strength (from 1.5 kN to < 0.5 kN, which is the difference from applying 200 kg of force to crushing with fingers) as seen in Table 4.11 when comparing the raw biomass (Date Pit Whole or DPW) to the processed samples. The date pits had become noticeably softer at less aggressive conditions (160 °C, 60 min), meaning that if the sole aim were to soften them for mechanical processing, then it can be done at lenient conditions. Coincidentally, the highest energy content estimate was from the same run, but there is a drawback that these date pits would be 10% heavier than date pits processed at 180 °C. And while the date pits would be losing 0.15 MJ/kg in potential energy content, there is the added benefit of larger quantities of liquid and solid yields generated under these conditions and leading to other income and energy streams.

Now though one of the aims of these trials was to separate the lignin fraction for use as a platform chemical source, this methodology has instead lead to removing a significant portion of mass while enriching the energy and lignin content. This is seen in the increasing mass lost from the original date pits (6.9 – 24.5%), while maintaining the estimated energy and lignin content (~19 MJ/kg and ~29% respectively) with increasing temperatures. Considering the experimental range is within the degradation temperature range of hemicellulose (150 – 250 °C), the mass loss that occurs in this range and coupled with the rising energy content data (from 18.4 to 19.1 MJ/kg), since cellulose and lignin both have higher energy contents than hemicellulose (16.5 – 18, 20 – 26 and 13.9 – 16 MJ/kg respectively), it can be deduced that the mass loss is attributed mainly to hemicellulose degradation. There may be some overlap with the cellulose fraction (200 – 450 °C) which may occur due to thermal runaway on a micro-scale but the controlled temperatures of the surrounding fluid would inherently reduce the chances of this occurring. More evidence of this may be present in the bio-oil extract where hemicellulose degradation products should be expected (aside from H_2O and CO_2).

DTA evidence of the degradation of the hemicellulose fraction can be seen in Figure 4.18 below, with focus on region **1**. When compared to the raw biomass (DPW), the hemicellulose peaks/shoulders can be seen becoming gradually smaller with increasing temperatures. That is to say that the degradation rates of the hemicellulose components occur at a faster pace if there is more of it when reaching the optimal pyrolysis temperatures. So at 150 °C, not enough hemicellulose had broken down that the peak in region 1 had a similar height to that of the raw sample (~0.2 %/°C), although the resolution of that same peak was better at indicating that the substance in question had become “purer”, also evidenced by the slightly higher peak which is also what is occurring in region **2** as the cellulose fractions become more isolated and disconnected from the hemicellulose and lignin. In region **1**, the peaks that were present up to 160 °C trial can be seen melding into the main region **2** peaks at 170 °C and is completely gone at 180 °C, marking the breakdown of hemicellulose as a whole bio-polymer into its sugars and by-products that more likely fall into the cellulose pyrolysis region (Region **2**) such as xylose and fructose. Figure 4.19 shows this same pattern happening as a function of time at the highest temperatures (180 °C), the progressive shrinking of the hemicellulose peaks can be observed in the 150 – 250 °C range as they gradually flatten or blend into the main cellulose peak. This is an indication that hemicellulose is much more readily degraded while in slightly less time than reported (≤30 mins in this study vs. ≤ 60 mins (Delbecq et al., 2018)) without the use of catalysts or recycling of the processing solution as used in the reference material.

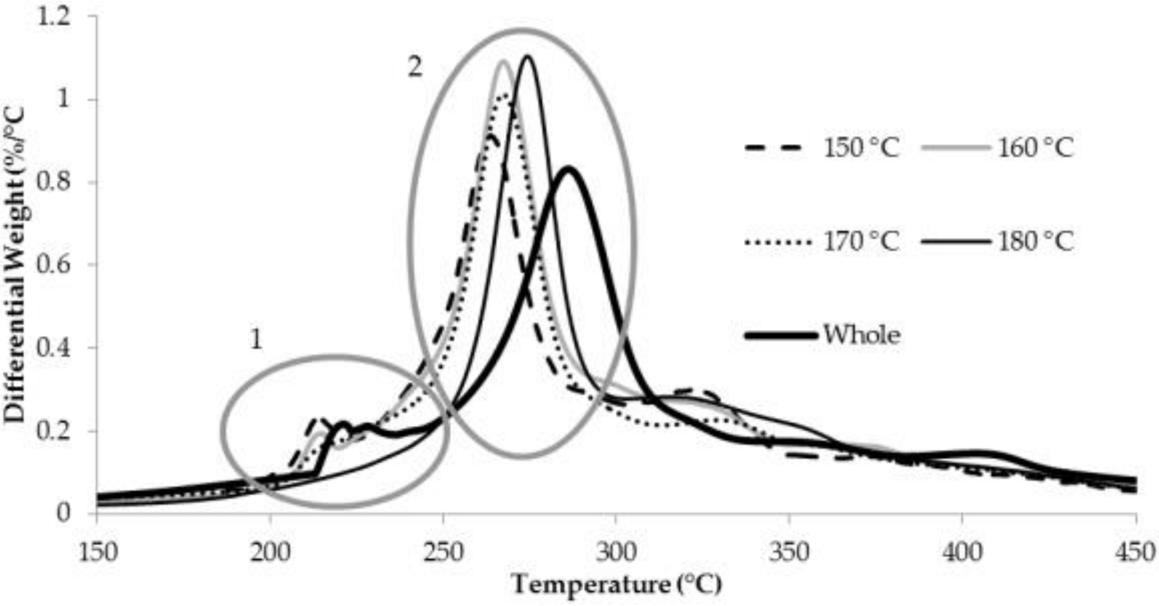

Figure 4.18 The graphical DTA data of the 45 min samples, where the changes to the (1) hemicellulose and (2) cellulose regions are most obvious, in comparison to the raw sample, Date Pit Whole.

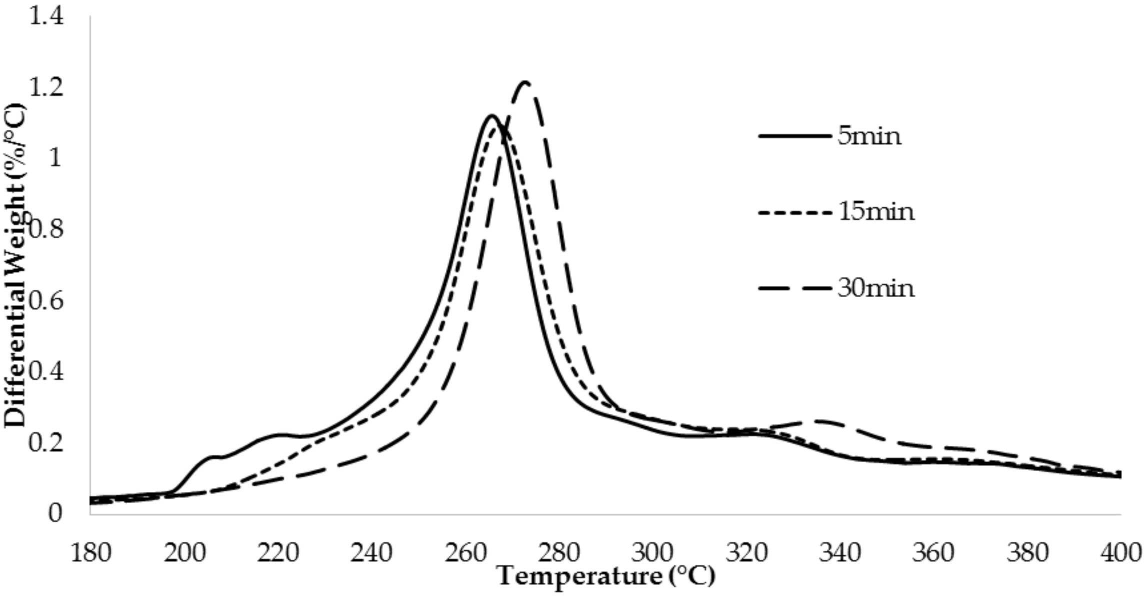

Figure 4.19 The DTA of 180 °C samples as a function of processing time.

The mass loss and degradation effects seen happening in this study are occurring at the earlier parts of the hemicellulose breakdown range, meaning that the links between cellulose and lignin are breaking down sooner. This allows these fractions to be liberated and purified without the anchoring of hemicellulose bridges to bind them to the overall lignocellulosic structure, giving rise to enriched sugar and phenolic fractions as solid or liquid yields. This is also evidenced in the TGA/DTA data as it shows the hemicellulose peaks in the raw date pit (DPW) do not occur/drop off until within the 200 – 250 °C range. The date pits have been softened (evidenced by the point load drop from 1.5 kN to < 0.5 kN) and enriched in terms of energy and fixed carbon content at lower temperatures than reported (150 – 180 °C). The TGA evidence suggests that the hemicellulose fraction is the part that had been pyrolysed out mainly in the date pits under the harsher conditions set in these experiments and thus, by finely cutting out the hemicellulose fraction (which is stated to be ~20% (Bouaziz et al., 2020)), the date pits can have upgraded cellulose/sugar and lignin/phenolic fractions. Combining the obtained data (~6% moisture content) and reference material (~20 hemicellulose), it can be assumed the most of the hemicellulose in the processed date pits had been pyrolysed at 180 °C and 60 minutes (for a total of 26% mass lost).

Based on the data presented, a hypothesis can be built that is split into 3 parts; based on the degradation patterns and rates:

1. The temperature conditions (150+ °C) and heating rate of the microwave method (800W+) initiate the degradation of hemicellulose into highly microwave sensitive/lossy products such as furfural.
2. Due to the internal and external pressure conditions of the date pit, the water remains liquid, gaining properties that encourage furfural dissolution in the moisture contained in the date pits. Eventually flowing out into the hydrothermal solution and forming the bio-oil fraction.
3. The microwave energy used to maintain the thermal conditions is selectively heating these products, and accelerates/propagates hemicellulose degradation by induced thermal runaway that is quickly quenched and dissolved further by the surrounding fluid.

4.2.2. The Solid Extract/Lignin Powder

As discussed in 4.2.1, the solid red brown powder extract yield was low (depicted below in Figure 4.20).

Figure 4.20 The solid red brown phenolic/lignin rich extract obtained from hydrothermal microwave extraction.

Expectations were drawn from research by Zheng et al. using bamboo, where they extracted a maximum of 4.8 g/L of lignin from bamboo biomass. However, despite these expectations, the methods used produced 0.46 g/L (6.966 mg) of solid extract/"lignin" powder (solid extract results are presented in Table 4.12), which is assumed to be 100% lignin (2016) before analysis and is significantly low in comparison to producible quantities shown in the research.

Table 4.12 The solid extract yield results of the hydrothermal microwave extraction, - denotes no solid yield was obtained. In brackets is the mass obtained as a percentage of overall date pit input mass.

Time (min) **Temp (°C)**	**5**	**15**	**30**	**45**	**60**
150	-	-	-	-	-
160	-	-	-	-	-
170	-	-	-	-	3.574 mg (0.4%)
180	-	-	-	0.704 mg (0.1%)	6.966 mg (0.7%)

Py-GC/MS and TGA analysis of the extracted powder (see

Table 4.13 and Table 4.14 respectively) reveals that a significant portion of the solid powder is phenolic-based. The presence of a large percentage of aromatic and phenolic products (not including the potential acetic acid, CO_2 and H_2O that could have formed from further pyrolysis) is evidence of how much lignin is in the solid extract based on Py-GC/MS analysis. These results also indicate that this much lignin or phenolic content had not recalcitrated back onto the date pit, as is a common occurrence in hydrothermal treatment (Pu et al., 2013). However, due to the small quantity of "lignin" powder obtained, it is unclear if this is an occurrence caused by the use of microwave heating, and further study would need to be conducted that would first address the yields and then the effects. The presence of this solid extract shows potential to improve yields without the use of environmentally damaging elements, since this method does seem to at least take some of the lignin extract and deposits it separate from the date pits as potentially long chained bio-polymer residues. There is still the issue of low solid extract yields which seems to be a drawback of this methodology however it is important to note that at $650/MT, at the minimum purity this yield has potentially significant value in larger quantities and can be considered as part of an income stream should this pre-processing method be improved upon. Despite this, hydrothermal pre-treatment is still effective at lower temperatures to soften the date pits and prepare them for more effective lignin extraction methodologies.

Table 4.13 Classification of the pyrolysates obtained from Py-GC/MS analysis of 0.5 mg solid extract (lignin powder) from the hydrothermal extractions at 180 °C, 60 min (left), compared to the Date Pit Skin (DPS) pyrogram data (right).

Group Component	% Composition from Pyrogram	
	Solid Extract	**DPS**
Short-chained compounds (> 2C, ≤6C)	3.83	12.16
Furans (4C, 1O rings)	1.5	9.44
Glucose related compounds) / Pyranoses (5C, 1O rings)	0.87	13.09
Aromatics and 6C rings	72.56	51.09
- Catechol	**37.67**	**13.93**
Long Chained Organic/Fatty Acids (> 8C)	21.26	14.21

Based on the energy content of pure lignin being ~21 MJ/kg, another drawback to this solid extracts low yield is that, despite its significantly higher energy content, cannot provide by itself an alternative energy route since the quantity generated cannot compare to the quantity of date pit residue that can provide similar energy yields. Instead it is suggested that the extract be used solely for renewable and environmentally sourced phenolic platform chemicals and biopolymers, and that a post-treatment method be developed to increase the yield such as ethanol extraction.

Table 4.14 Proximate analysis of the solid extract in comparison to the raw date pit and the sample it was extracted from.

Sample ID	VM	FC	Ash	HHV (MJ/kg)	Lignin %	Strength (kN)
Date Pit Whole	77.45	21.84	0.71	18.40	19.8	1.5
180 C, 60min	73.34	25.64	1.02	19.14	28.3	<0.5
Solid Extract	63.19	35.08	1.73	21.00	46.9	---

A key highlight from the proximate analysis of the solid residues of the date pit and solid extract (Table 4.14) is that there is a sizeable amount of lignin that had either precipitated or remained in the date pit, but the concentration of which has risen and thus leading to enriched cellulose and lignin fractions in the date pit while capturing a small amount of lignin extract in the form of reddish-brown powder. There is also the possibility that some of the potentially extractable lignin has dissolved in the hydrothermal solution as occurred in previous studies, required acidic treatments to precipitate them out (and inadvertently degrading them to lower value lignins) (Zheng et al., 2016). This will be examined next but for now, it seems that the expectation to extract a reliable quantity of lignin powder has not been achieved without the use of a secondary extractive solution, though it remains plausible and needs further investigation.

4.2.3. The Bio-Oil Extract

The hydrothermal process also yielded low quantities of bio-oil (examples of which are seen below in Figure 4.21), which ranged from being a clear yellow liquid to cloudy, heterogeneous red-brown solution. Upon extraction with 7 date pits a sufficient amount to allow analysis was collected (6.3% of input mass). The freeze dried bio-oil was very tar-like while the oven dried bio-oil was collected as a solid (much like caramelised sugar). Therefore Py-GC/MS remained as one of the viable analytical methods for this residue, the results of which are shown in

Table 4.15. These results are meant to report both the contents of the bio-oil obtained from hydrothermal extraction as well as observe the differences between oven drying and freeze drying the bio-oils in terms of component maintenance. It is vital to note that both drying processes may have led to a loss in many of the volatile pyrolysis products such as low weight alcohol and ketones. The bio-oil extracts for the 180 °C runs are shown in Figure 4.21.

Table 4.15 Py-GC/MS analysis of the 0.25 mg of bio-oils extracted from 180°C 60 min sample (done in duplicate), comparing the methods meant to remove residual water and lighter volatiles from the extract.

Group Component	% Composition from Pyrogram	
	Oven dried bio-oil	**Freeze dried bio-oil**
Short-chained compounds (> 2C, ≤6C)	41.96	17.57
Furans (4C, 1O rings)	22.92	16.53
Glucose related compounds) / Pyranoses (5C, 1O rings)	13.98	20.41
Aromatics and 6C rings	12.95	29.10
- Catechol	**8.35**	**11.29**
Long Chained Organic/Fatty Acids (> 8C)	8.17	16.18

A few things can be pointed out in these results. First: the quantity of components is more spread out towards the heavier yields in the freeze dried samples as opposed to the oven dried samples, which contain a significantly higher amount of short chain compounds. This encourages the use of freeze drying to maintain the content of the bio-oil for future studies. Second: regardless of drying method, it is apparent that the phenolic content is overall higher in the bio-oil than the in the solid extract (4.2 – 9.4 % in the bio-oil compared with 1.2% in the solid extract), thus a good quantity of phenolics is present in the bio-oil and may require additional steps to extract efficiently. This method can be considered unfinished with regards to lignin separation without adding environmentally malignant methods. However, it should still be noted that the vast majority of lignin has not even been extracted from the source date pits, while clearly the sugar content has at least seeped into the water as degradation products (such as acetic acid, furfural, furan and pyranoses) as well as some of the lignin but still not enough to consider the bio-oil fraction a reliable source of phenolics without improvements. It may however be used as a source of additives for the petroleum industry of Oman or as a source of bio-ethanol.

While it is unclear why the drying method affects the heavier yields, a possible hypothesis is that freeze drying maintains more of the lighter fractions. When the samples are exposed to the Py-GC/MS pyrolyser, the breakdown of larger molecules does not contribute as much to forming more minor compounds as oven drying since most of the smaller, light weight compounds may have vaporised, leaving behind essentially a heavy tar-like oil.

Figure 4.21 The bio-oil in water extracts at 180 °C, processing time from left to right: 5; 15; 30; 45 and 60 minutes. Showing the drastic change in colour and solids content suspended in solution. They all smelled strongly of caramel.

Based on the overall results of this section; with regards to lignin extraction, the mass balance of the lignin based on estimation and Py-GC/MS analysis is calculated as shown in Table 4.16. It can be seen that the main aim of the method had failed in that solid lignin powder or a significant lignin yield could not be obtained however most of the extractable lignin remained in the date pit as an enriched fraction. And the bio-oil turned out to contain most of the extracted lignin (even in the oven dried bio-oil), but this can be removed in secondary steps such as fractional distillation or acid precipitation.

Table 4.16 The mass balance of lignin as calculated using the yields of date pits processed at 180 °C and 60 min. It shows that while the expectation of this method was to extract lignin as a solid powder in significant quantities, the actuality is that most of the lignin that extracted had dissolved into the bio-oil.

Sample ID	Raw Date Pit / DPW[1]	Processed Date Pit[2]	Solid Extract Powder[2]	Bio Oil (Freeze Dried)[2]
Lignin/ Phenolic Content (%)[3]	19.8	89.4	1.20	9.4

Although one of the main aims of this process was to separate the lignin heavy skin from the date pit was not achieved, the positive outcomes from this negative result are the augmented husks. Using the presented evidence based on proximate and Py-GC/MS analysis of the yields, there is a strong likelihood that the majority of the hemicellulose fraction in the raw date pits (not quantified due to time and scope constraints, assumed to be ~20% (Bouaziz et al., 2020)) had degraded and formed the pyrolysis oil yield. It is likely that the microwave radiation and high temperatures caused thermal degradation and charring in the date pit. This leaves behind a date pit husk where the remaining lignin fraction which was unaffected by the hydrothermal process due to its thermal stability, and had increased in concentration from 19.8% up to 30% of the overall date pits mass. This fraction can then be treated with alternative post-treatment methods to extract the phenolic fraction at a potentially faster rate, since the hemicellulose linkages have broken down and due to a significantly lowered point load, the date pits became easier to break mechanically. This will help maintain the quality of the latent platform phenolics in future processes. The remaining cellulose portion, being more thermally stable than hemicellulose and showing a high presence in the DTA data of the husks, presents a viable quantity of cellulose (albeit charred) ready for use in other industries. Cellulose, which is essentially long glucose chains that can then be used for fermentation processes to make bio-ethanol fuels or as a higher energy animal feed since the raw date pits powder was initially used as broiler feed. The extracted yields (bio-oil and solid powder) have significant potential as secondary product streams but the low quantities obtained in this study suggest more work needs to be undertaken to optimise yields while maintaining environmental standards.

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[1] As a percentage of the raw date pits overall mass.

[2] As a percentage of the initial content found in raw date pits.

[3] Dry, ash free and extractives free basis.

4.3. Microwave Pyrolysis Results

Microwave pyrolysis was used in this study to observe the behaviour of relatively dry biomass in this process. Microwaves in this setting would affect the water molecules, causing them to vibrate rapidly and generate heat as an energy loss mechanism. Since the water is contained in microwave transparent, lignocellulosic biomass, it can potentially reach higher temperatures due to increase in intracellular pressure that would maintain its liquid form in high temperatures (> 100 °C). The objective is to test how this behaviour can be exploited to generate biomass degradation products that can potentially substitute crude oil as an energy and platform chemicals source. The hypothesis for this methodology is that the few water molecules would undergo significant microwave loss effects, triggering a chain breakdown mechanism within the biomass as hemicellulose is exposed to the trapped high energy water molecules; which would then lead to formation of hemicellulose products that are also microwave sensitive and that the application of direct microwave energy would require significantly less energy input as a result of this chain of events. This would hopefully lead to a high yield of bio-oil while incidentally preserving the thermally stable fractions of the date pit. By adjusting the heating rates and thereby the electric field, the results obtained may be reflected in the loss behaviour of the moisture and pyrolysates and production rates of the residues. The outcomes of this process were expected to produce yields under similar conditions of fast pyrolysis: good bio-oil yields with highly charred biomass. It would be interesting to see what results a direct pyrolytic approach would yield in terms of quantity and composition of the bio-oil fraction. These will be discussed and analysed in this section.

The main reason the higher powers were not tested were due to complications occurring in some of the 700W tests, where an excess of heat or pressure would break seals and some of the pyrolysis vapours escaped into the environment. There was also a case where an arc had occurred in the date palm biomass due to excess carbon in the sintered disk, causing a flash pyrolysis condition where large and hot amounts of pyrolysis oil and vapour blew the nitrogen funnel off the reaction vessel.

4.3.1. The Pyrolysis Conditions and Results

4.3.1.1. Pyrolysis of Whole Date Pits

The pyrolysis of the date pits generated 2 products that were collected: a charred date pit husk, with some remaining unprocessed depending on the energy input and random packing affecting the penetration depth of the microwaves; and the bio-oil vapours that were produced as a result of rapid heating of lignocellulosic material. In some extreme cases, where arcing was observed, the bio-oil vapour had evolved too rapidly to be effectively collected by the condensation apparatus. The initial results of the experiments (performed in triplicate where possible) are presented in Table 4.17 below.

Table 4.17 The extracts of dry microwave pyrolysis (measured in triplicate where possible). In brackets are percentages relative to the input amount.

Applied Power (W)	Mass Before (g)	Mass After (g) (Loss %)	Bio-Oil Yield (g) (%)	Absorbed Energy (kJ/g)	Time until P_{abs} <10% (s)
100	10.4519	7.7255 **(26.1%)**	0.5709 **(5.5%)**	3.40	572
200	10.2502	7.0350 **(31.4%)**	1.3610 **(13.3%)**	2.40	273
300	7.7140	5.472 **(29.3%)**	0.6892 **(8.9%)**	2.53 ± 0.71	176 ± 12
400	9.9513	7.0808 **(28.8%)**	1.5149 **(15.2%)**	2.65	169
500	7.2122	3.6136 **(49.9%)**	1.6070 **(22.3%)**	2.76 ± 0.22	85.7 ± 5
600	10.4847	5.0368 **(52.0%)**	2.7973 **(26.7%)**	1.92	87
700	7.5583	2.6269 **(65.2%)**	2.3789 **(31.5%)**	2.78 ± 0.27	78.5 ± 2.5

The “**Time until P_{abs} <10%**” or processing time is considered the threshold for completion, not only for safety reasons but mainly because the biomass was considered charred, completely pyrolysed and would not produce more collectable vapour or data. As the input power had increased linearly, the processing time had decreased at an exponential rate and was tapering off at over 75s by the maximum power conditions.

Meanwhile despite the process time and power input changing drastically, the calculated absorbed energy had remained in a stable range throughout the experimental conditions

The mass loss trends in this study can be used to observe the effects of power and to compare to hydrothermal processing in terms of changes made vs. yields obtained, allowing the researcher to trace the behaviour of date pits under microwave effects with regards to fixed carbon content, potential caloric values and presence of less thermally stable sugars (hemicellulose chains). During experimentation using the microwave generator, the applied power from the generator was monitored and terminated as required for safety and equipment maintenance purposes. That is to say when the experiment called for using 500W, the biomass would absorb ~250W which decreased as the bio-oil and moisture evolved from the biomass. Lowered absorption is a general indication of carbonisation and can lead to a sudden spike in absorbed power, which can subsequently lead to arcing and thermal runaway that can damage the glassware and equipment and produce large uncontrollable quantities of bio-oil vapours. The absorption pattern can be observed in the compiled chart presented in Figure 4.22 where the absorbed energy was plotted over time and terminated where the absorbed power is about ≤10% of the applied power.

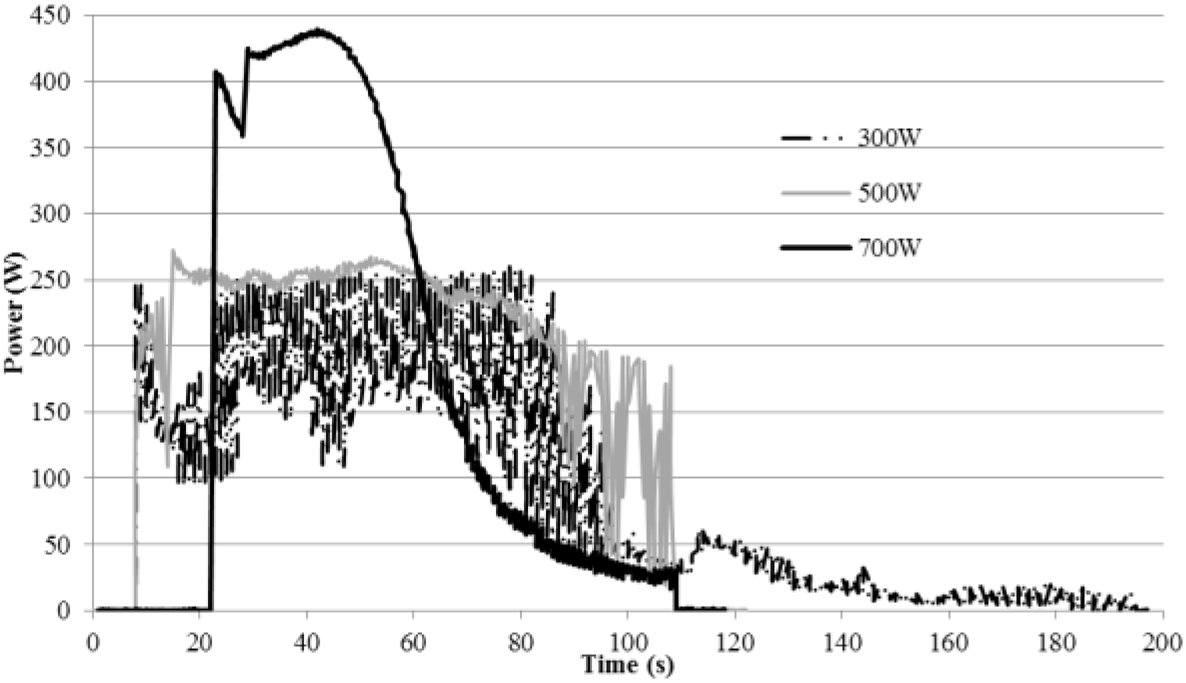

Figure 4.22 The absorbed power plotted versus time for 3 power inputs: 300W, 500W and 700W

To summarise, the time taken for the absorbed power to reach ≤10% of the applied power is noted as the processing time, as further radiation could lead to full carbonisation in charred areas of the biomass which could eventually lead to arcing that can damage the equipment and invalidate the data. Despite the subjectivity of this method, there was an obvious exponential trend for the processing time to decrease as the applied power increased; indicating that the experimental design is very sensitive to power intensity as seen in Figure 4.23.

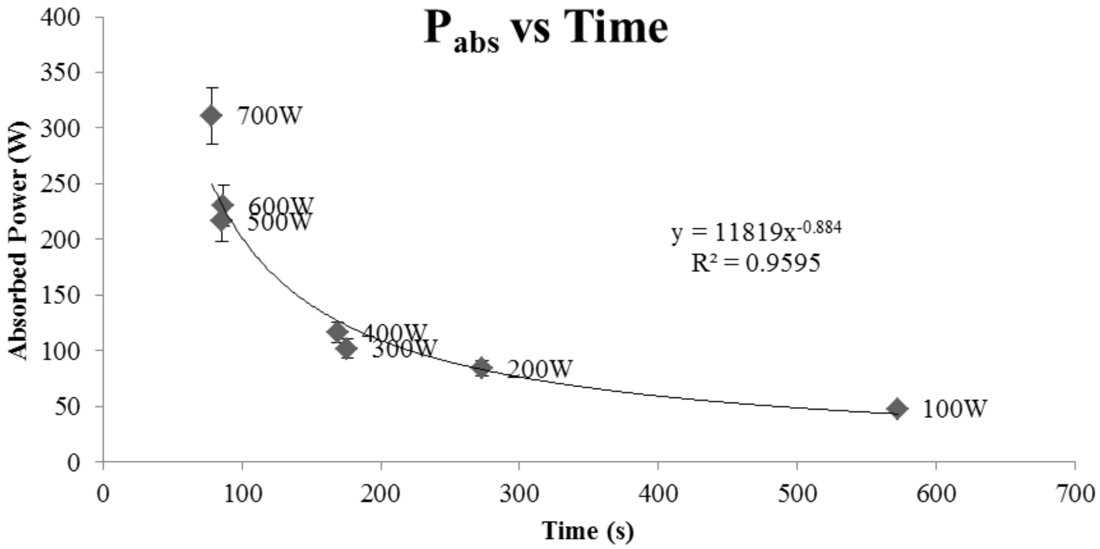

Figure 4.23 The exponential behaviour of the average absorbed power versus the processing time can be seen here. The data points are labelled by the initial input power, while the average absorbed power is usually <50% of the input.

Studying the effect the absorbed energy has on the biomass would prove to be a challenge as when measured, the energy remains steadily within the range of 2 – 3 kJ/g across all power inputs as can be observed in Figure 4.24. Though there is an obvious but small steady increase while increasing the input power variable, it is important to see whether the power or energy has an impact on overall yield of bio-oil. Assessing the significance of this data and testing it will be handled in future sections.

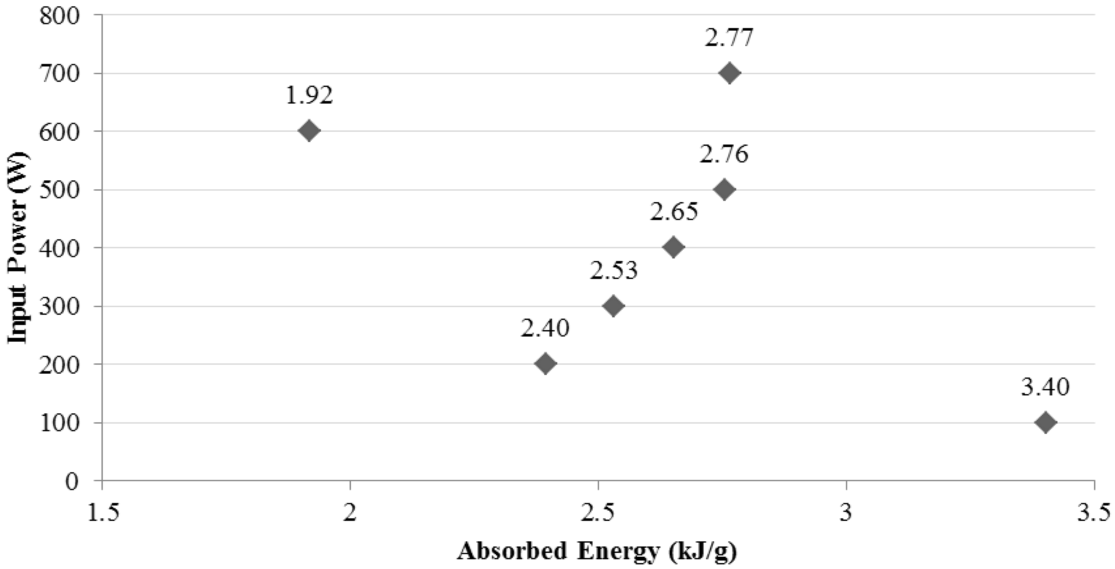

Figure 4.24 The measured energy absorbed by the biomass versus the input power at each power interval.

Collectively, this data shows that even with a relatively dry biomass sample, the microwave energy can be absorbed enough to induce heat loss and pyrolyse the date pits with varying effectiveness depending on the applied power which is reflective of the heating rate. However, the absorption pattern remains similar in that it can start relatively high (~50% of applied power) and gradually drop off to <10% once the intrinsic moisture and microwave sensitive volatiles have been liberated from the lignocellulosic structure. This is especially evident in the 700W sample, as it loses the majority of its absorptivity after 40s of microwave radiation. At the same time, a higher applied power should in theory lead to higher amounts of energy converted and absorbed from losses, which may be an explanation for the higher bio-oil yields and mass losses.

While observing the whole pit tests, there is a spike in mass loss and bio-oil yield at power inputs higher than 400W (See Figure 4.25), increasing from ~30% to ~50% in mass lost between 200W and 500W while also increasing bio-oil yields. The mass loss contributed also to softening the date pits, with the fully processed date pits requiring < 0.5 kN to crush in a point load (down from 1.5 kN).

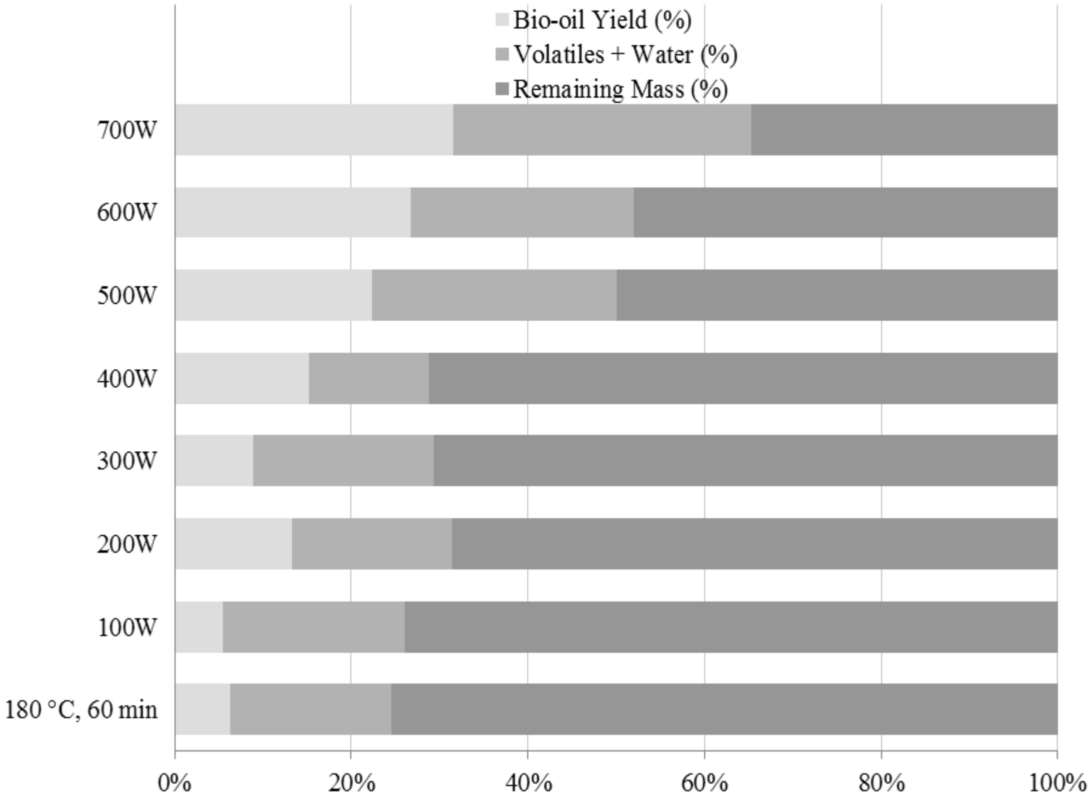

Figure 4.25 A bar chart representing the bio-oil yield, volatiles that did not condense and residual mass after each power input condition. The harshest condition hydrothermal results from the previous section are at the bottom for comparison.

This is adding to the question of whether it is the power input or the absorbed energy contributing to the increase in bio-oil yield and mass loss. However it is worth nothing that at the lowest power input (100W), the results are directly comparable to the highest hydrothermal conditions (180 °C, 60 mins) in that the date pits have lost a similar amount of mass to volatiles and bio-oil production. Indicating that far less energy and time can be spent to get similar results as the previous method, albeit without a phenolic rich solid extract.

In Figure 4.26 below, the bio-oil yields are plotted versus the absorbed energy, with the circled area indicating the range of values obtained when calculating the absorbed energy per gram of date pits. The circled area corresponds to a range between 2.4 – 2.8 kJ/g of energy absorbed by the unchopped date pits.

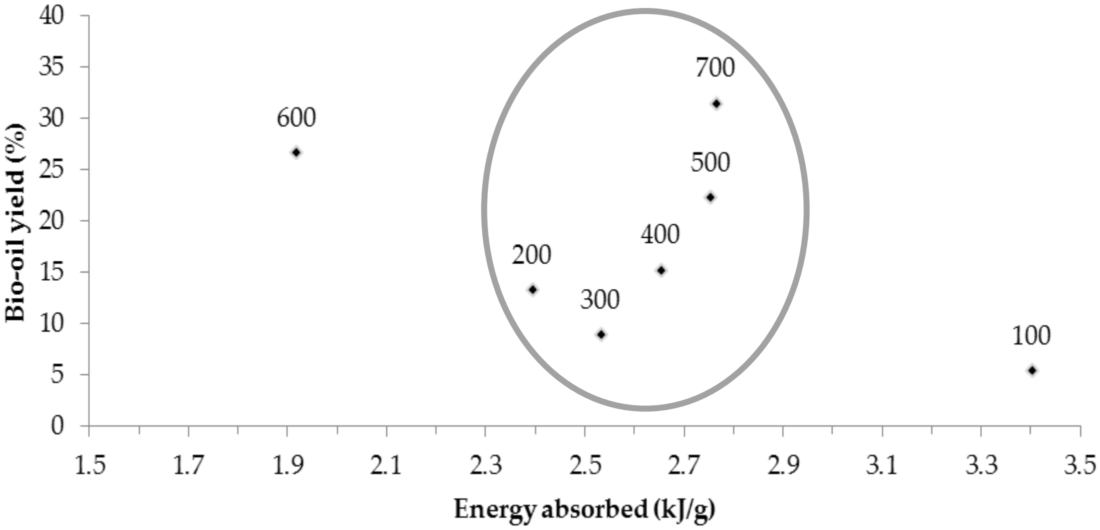

Figure 4.26 Plot of the bio-oil yield versus the energy absorbed per mass of each test. The circle shows the range where most of the data points hover within with a few outliers in each group.

Based on the data provided, it can be seen that despite the 100W absorbing the most overall energy throughout the process, this condition has produced the lowest yields of extractables from the date pits other than the date pit husk. It should be noted that although it did remove a sizeable amount of volatile material from the date pits, the 200 to 400W powers had produced similar mass losses while also producing more collectible bio-oil yields and also at significantly faster rates. From 500W upward, there is a noticeable increase in yield and mass loss and an overall substantial dip in the absorbed energy for all the powers greater than 100W. Adding to this, when calculating the average absorbed power for each test versus the time which is exponentially decreasing for every 100W is a clear indication that microwave bio-oil production is mainly controlled via heating rate induced by dielectric loss than by overall energy absorbed throughout the microwave process (refer to Figure 4.26). The 600W and 100W points are not necessarily outliers in that they produce yields in expected areas but the amount of energy they absorbed may not be as accurate as hoped. Based on the exponential data, it can be deduced that if maximum pyrolysis conditions have not been reached, they are not far off from 700W.

These details point toward a maximum input power for the laboratory scale experiments (between 500W and 800W) vs. yield which could be investigated further in larger scales. The 700W trial also indirectly reveals a high degree of carbonisation as the remaining mass (34.76%) is moving towards the fixed carbon content (21.84%) obtained in proximate analysis of raw date pits (refer to Section 4.1.1, Table 4.1), assuming most of the phenolic content had not pyrolysed under these conditions. Whereas the 100W results display similarity in mass loss (26.1%) and bio-oil yield (5.46%) to 180 °C, 60 min hydrothermal conditions (24.5% and 6.3% respectively), and showing possibility of similarity in content, behaviour and quantity. This is encouraging the use of this method if the main goal was obtaining a bio-oil fraction while softening the date pits significantly, as this could be achieved in a matter of minutes depending on the vessel size and volume of sample.

Hypothetically, based on the mass loss patterns, bio-oil quantities and energy calculations, it is apparent that at lower powers, the heating rate is slow enough that generated temperature increases generated via microwave heating can pyrolyse the lower energy components such as hemicellulose and xylans on a micro-scale (to be investigated further upon analysis of some of the bio-oils). As the power increases, there is a higher chance the cellulose fractions and some of the lignin fractions pyrolyse and degrade due to the rapid accumulation of heat generated as a result of the dielectric losses within the biomass, propagated by the trapped moisture and hemicellulose pyrolysates that have yet to volatise.

4.3.1.2. Effect of Energy Input

The results from Section 4.3.1.1 suggest that power input is the main factor in producing the greater outcomes such as pyrolysis bio-oil quantities and charred date pits. This section has decoupled the power input and absorbed energy to confirm this by testing under the following conditions:

- Constant power, changing the amount of energy absorbed by the biomass.
- Constant energy input, changing the applied power and thus changing the energy absorption rate.

In the chart below (Figure 4.27), dry date pit biomass is shown to display microwave absorptivity. This chart reveals 2 key points: 1) Date pits absorb about 50% of the applied power from microwaves before dropping off and 2) as they pyrolyse, they lose a significant amount of their absorptivity as the biomass degrades into bio-char and other products, with large variation in the final 30s of processing, possibly due to carbonisation in some parts. This absorption can be translated into loss which is basically how much microwave energy is converted into heat. Almost 20 kJ of total energy had been absorbed by the overall biomass during treatment, as a result of absorbing 10 – 50% of the applied power over time. The variation seen in the last 30 seconds of each run can be explained as two possibilities occurring simultaneously:

- Carbonisation, leading to momentary microwave transparency occurring mid-processing inside the date pits.

- Formation of bio-oils which are generally microwave transparent as vapour but can be very absorbent as liquid, however during pyrolysis the date pits unseal and evaporate the more volatile matter as water or bio-oil residue. And what remains (bio-char) does not contribute heavily to microwave heating either.

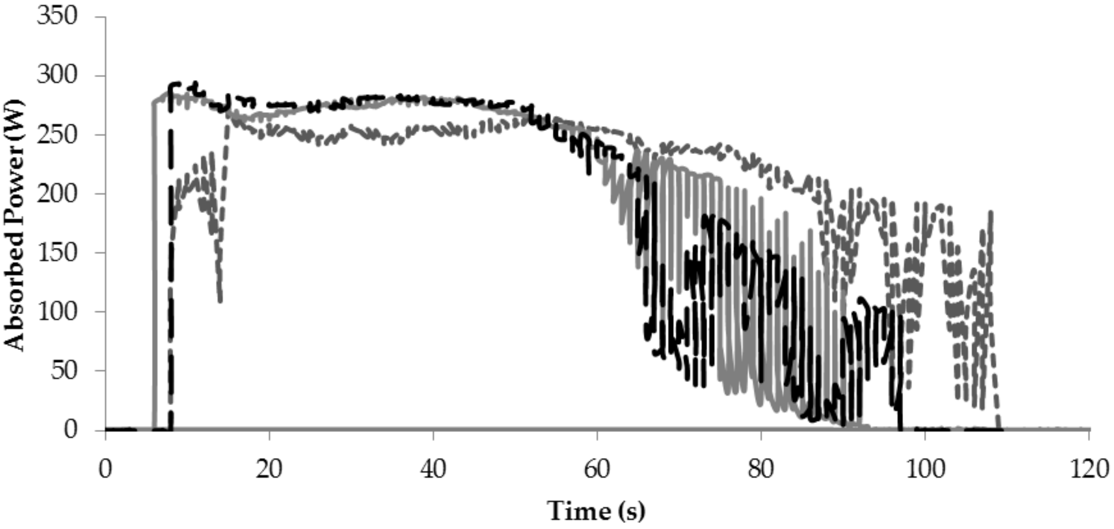

Figure 4.27 The absorbed power chart of the 500W experiments (Done in triplicate).

The above theories were further tested by implementing information obtained from the tests such that: different input powers were used to reach specific absorbed energy limits (~2.0 kJ/g in this case) to test the effect of microwave input power (See Table 4.18), and using 300W as a stable input to observe the effect of energy input as a function of time (see Table 4.19).

Table 4.18 Obtained and calculated results of the energy input experiments. Aiming for 2.0 kJ/g was harder than expected due to variability in the biomass samples.

Pi (W)	Actual Time (s)	Average P_{abs} (W)	Energy absorbed (kJ/g)	Bio-Oil Yield (%)	Mass loss (%)
100	416	51	2.29	14.13	31.32
200	241	71	1.77	15.92	27.18
300	195	96	2.01	13.26	23.19
400	183	187	3.63	27.25	48.72
500	88	180	1.80	18.9	33.67
600	84	207	1.96	22.5	42.81

While the aim was to ensure that roughly 2.0 kJ/g was absorbed, the 400W test proved to be the unstable run and the results at 400W are therefore anomalous. Despite this however, it displayed the expected behaviour, with bio-oil yield generally increasing as the energy input rate (i.e. applied/incidental power) increases. This does however show that the absorbed energy does contribute to a certain degree toward bio-oil production, as shown in the data below (Table 4.19) where a good amount of bio-oil was obtained at higher absorbed energies (1.99 kJ/g to produce 20.32% of bio-oil). The main issue with this is that since this parameter is dependent on the microwave absorptivity of the biomass, it would be difficult to control and ensure the appropriate amount of energy is absorbed to produce optimal yields.

Table 4.19 Results of the constant power, varying energy absorbed experiments to observe the effect of energy input on the date pit treatment.

Pi (W)	Actual Time (s)	Average P_{abs} (W)	Energy absorbed (kJ/g)	Bio-Oil Yield (%)	Mass loss (%)
300	54	133	0.79	0	6.5
300	112	76	0.90	4.55	11.89
300	161	71	0.96	5.11	10.61
300	205	79	1.79	20.52	37.87
300	260	67	1.99	20.32	31.98

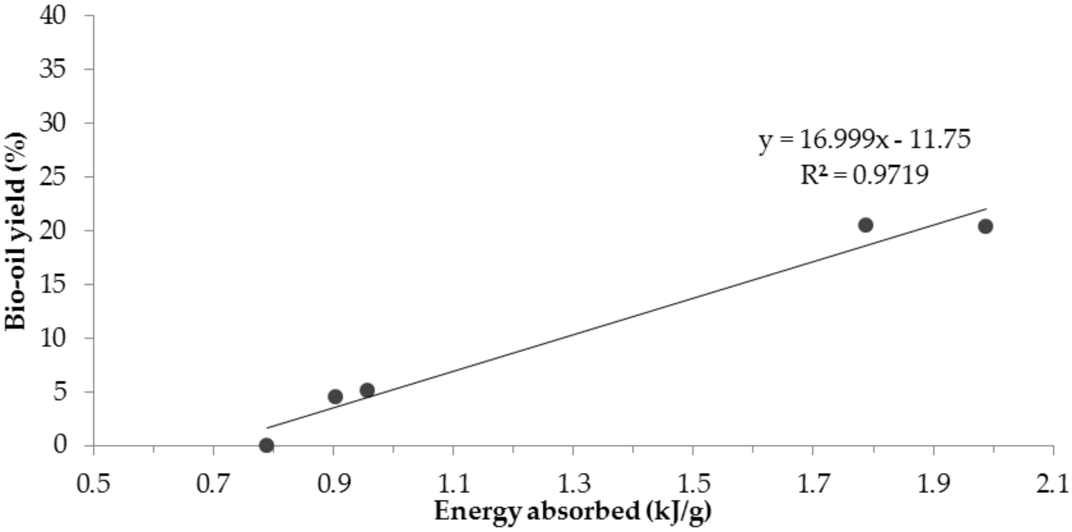

Figure 4.28 The results from charted to better show the almost linear relationship between bio-oil yield and absorbed energy. Fluctuations would be due to the random make up of the input biomass.

Based on the data analysis, a clearer picture can be made into the mechanism and effect of microwave energy in obtaining pyrolysis oil from biomass. The importance of superheating the moisture content at a higher rate so that it can have an opportunity to impact the surrounding bio-polymer material and break it down into more microwave favourable components and produce higher yields of bio-oil.

4.3.1.3. Effect of Sample Preparation

This was to test a hypothesis that (regardless of how dry the date pits were) whether moisture contributed to microwave pyrolysis and formation of bio-oil, thus by unsealing the date pits, the water had more freedom to escape and have a lower effect on yields.

Table 4.20 below presents the results of performing the power input trials on chopped date pits. It shows that the chopped have not lost a significant amount of mass in comparison to the unchopped samples (25.9% chopped vs. 26.1% unchopped), whereas they have managed to double the bio-oil yield (11.1% vs. 5.5% respectively) at 100W mark. This trend continues where unchopped produces greater yields while maintaining the mass loss degree up to 500W and above, where the mass loss does increase significantly for both but the bio-oil yield is slightly greater in the unchopped date pits (29.2% chopped vs. 31.5% unchopped) whereas the mass loss is significantly higher in the unchopped at 700W (55% chopped vs. 65.2% unchopped).

Table 4.20 The yields and data obtained from processing chopped date pits, to observe the effect of exposing the core.

Applied Power (W)	**Mass Before (g)**	**Mass After (g) (Loss %)**	**Bio-Oil Yield (g) (%)**	**Absorbed Energy (kJ/g)**	**Time until P_{abs} <10% (s)**
Chopped, 100	10.6250	7.8713 **(25.9%)**	1.1785 **(11.1%)**	2.92	577
Chopped, 200	8.9766	5.9194 **(34.1%)**	1.4343 **(16.0%)**	3.87	285
Chopped, 300	9.726	6.9647 **(28.4%)**	1.2733 **(13.1%)**	2.07	179
Chopped, 400	9.7494	5.4322 **(44.3%)**	2.0678 **(21.2%)**	3.65	151
Chopped, 500	10.973	7.4661 **(32.0%)**	1.4465 **(13.2%)**	1.37	73
Chopped, 600	10.2582	4.5897 **(55.3%)**	2.3963 **(23.4%)**	2.20	95
Chopped, 700	8.0017	3.5982 **(55.0%)**	2.3376 **(29.2 %)**	2.43	82

This seems to hold true in that there is a noticeable drop in bio-oil yield is some tests (35% less than uncut date pits at 500W), however when looking at the image below

(Figure 4.29) it can be seen that not all of the pieces had pyrolysed as well. This is suggesting that, due to fewer gaps in the overall sample the penetration depth of the date pits biomass had been reached at about 1.5 cm. This fact can be a contributor to the lowered mass loss in the chopped date pits, but it is not clear this is the only reason.

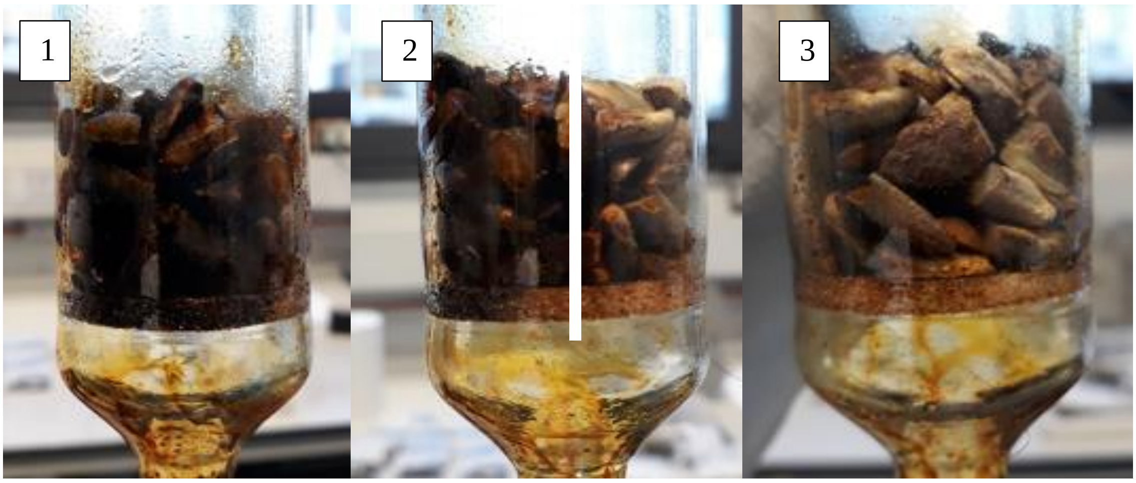

Figure 4.29 From left to right: 1) the charred side of the Chopped 500W date pits; 2) the side view with the white line indicating where the charring approximately ends, 3) and the unprocessed side of the same set. A visual representation of microwave penetration depth in date pit biomass and incomplete pyrolysis as a result of this.

Figure 4.30 below depicts the variation of the absorbed energy across the input powers using the chopped date pits. It can be seen there is no observable pattern in this set of results and no known relationship.

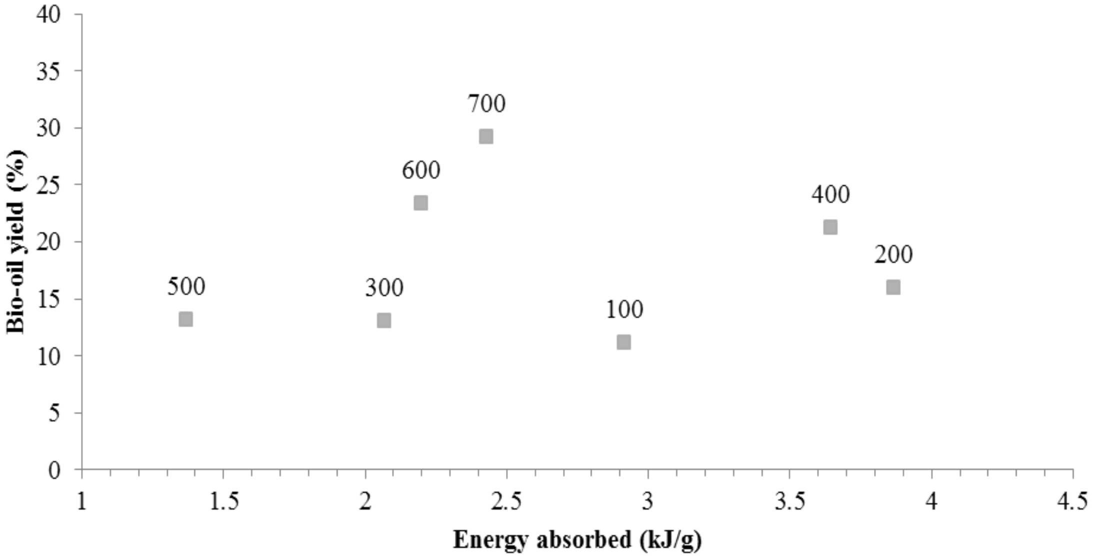

Figure 4.30 The bio-oil yield vs. energy absorbed at the labeled input powers.

When looking at the data from processing chopped date pits, the following comparisons can be made:

- Given the pits were halved; they only took slightly longer to process than the whole date pits.
- The overall absorbed energy was generally unstable for the chopped pits, most likely due to differences/randomness in packing, alignments and fewer gaps between the biomass fragments versus their whole counterparts. See Figure 4.30 for a visualisation of the variability in absorbed energy.
- While the bio-oil yield was higher at lower powers for chopped pits, it remained at a steady range at these powers and was essentially lower at higher powers than the whole pits.

These observations feed into the trapped water theory part of the microwave biomass pyrolysis mechanism, since the water now has an outlet to evaporate and escape from its natural containment.

4.3.2. The Processed Date Pit Husks

Moving on to examine the physical yields and upon analysing the whole date pit husks via TGA, interesting results were obtained (See Table 4.21). There is a huge jump in fixed carbon content just in the 300W run from the raw material, leading to a relatively big spike in energy content and lignin content, showing a connection to the hydrothermal results in how the fixed carbon content is related to the energy content, adding 1 kJ with a lighter overall weight. The hydrothermal results reflect the “Chopped, 500W” results very closely, keeping in mind that not all of the material had pyrolysed and so there may be some inaccuracies in this analysis. While the energy content of the 500W run is not abnormal considering it is getting closer to carbon (Carbon HHV = 32.8 kJ/g). It is also a consideration that the lignin content of this yield had not pyrolysed since it can contribute to increased energy content as well as the carbonised fractions in the biomass samples. The 500W sample also has a significant spike in carbonisation. Though it follows the increasing carbonisation with increased power trend, this result is particularly high and is likely due to the pyrolysis condition being extremely ideal for this sample to carbonise uniformly than in the 700W sample that would occur at a faster and less uniform fashion. With increasing powers there is a higher degree of carbonisation, which can theoretically lead to to higher potential HHV outputs as the biomass loses more volatiles and converts into fixed carbon over the microwave pyrolysis process.

Table 4.21 The TGA analysis of several trial powers to observe changes that occur from low to high MW Pyrolysis (MWP) in comparison to the raw material and hydrothermal (HT) extract.

Applied Power (W)	Volatile Matter (%)	Fixed Carbon (%)	Ash (%)	Moisture (%)	HHV (kJ/g)	Experiment Mass Loss (%)
Raw – DPW	77.45	21.84	0.71	4.09	18.40	---
MWP – 300	64.16	34.59	1.25	1.59	20.90	29.3
MWP – 500	39.79	57.52	2.69	3.13	25.39	49.9
MWP – 700	64.41	34.14	1.45	2.09	20.81	65.24
MWP – Chopped 500 W	72.66	26.02	1.33	1.18	19.22	13.18
HT - 180 °C, 60 mins	73.36	25.62	1.02	2.25	19.14	24.5

The differential analysis of the dry microwave pyrolysis samples tells another aspect to this story (Figure 4.31). It can be seen in the hemicellulose region that 300W and "Chopped, 500W" date pits still contain small amounts of hemicellulose that are being burnt out with increasing power, as these peaks are no longer present in the 700W husks. The 500W trial also reveals removal of cellulose/glucose from the date pit, implying that most of the sugars had pyrolysed and are present in the bio-oil yield. An indication that nearly all low energy volatile matter had been pyrolysed in the process and what was left behind is either carbon or lignin/phenolics.

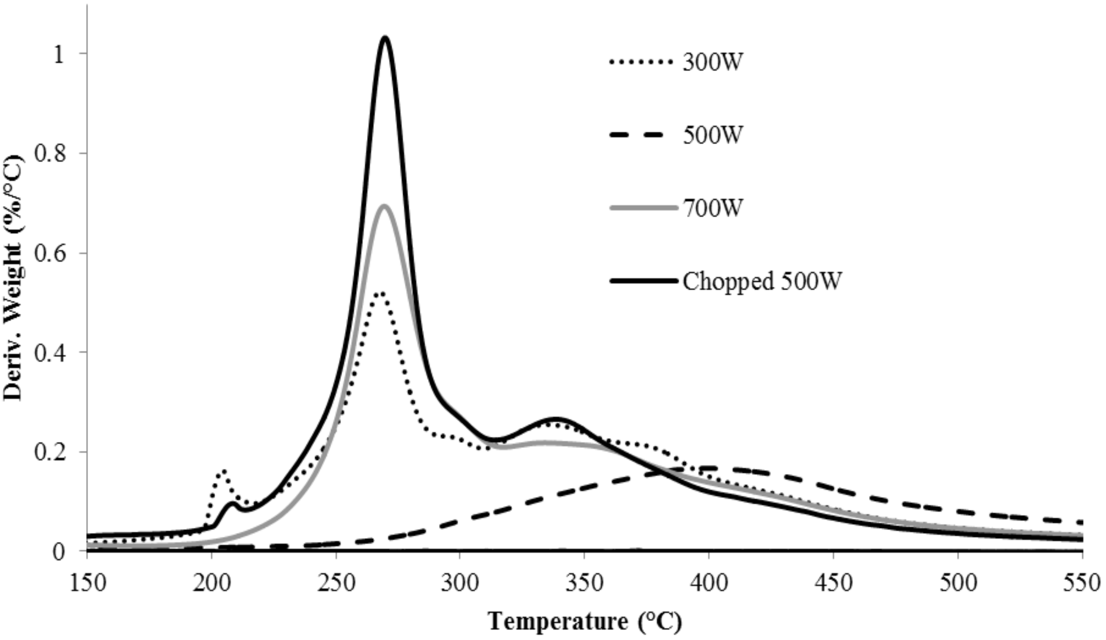

Figure 4.31 The differential thermal analysis of the date pit husks, showing the shrinking of the hemicellulose peak (between 175 – 225 °C).

The physical analysis shows how at higher powers, the energy absorption rate contributes to the degradation of the hemicellulose fraction. As seen where the hemicellulose peaks are not present in the whole 500W and 700W tests. This makes sense given the amount of mass loss/degradation the date pits had during the experiments. What is important to note is that in the whole 500W run, the cellulose peak had shifted over to the phenolic range, indicating potential thermal runaway in the particular sample and pyrolysis of the cellulose components.

In conclusion of these results, after examining the effects of the three parameters on the date pit biomass under direct microwave radiation and fast dry pyrolysis conditions, several points are made clear:

- At higher powers for whole date pits, heating rate is influenced through the dielectric loss tangents of trapped moisture and hemicellulose products. Leading to selective and rapid heating of these materials and higher loss tangents than the surrounding biomass form and further break down of lignocellulosic components into bio-oil and vapour.

- Smaller particles (chopped date pits) prevent microwaves from penetrating deeper into the samples due to packing, reducing the overall bio-oil and bio-char yields and leaving most of the biomass unprocessed and as hard as it began.

- While energy input/absorbed energy does contribute to pyrolysis yields at lower powers due to heat transfer processes being given time to catch up with the selective heating occurring in the moisture content. It is not a significant contribution compared to heating rate/incidental or applied power. This is again likely due to the selective heating phenomena that can directly provide high amounts of energy in small time frames at random points in the biomass sample; ensuring large enough amounts of biomass undergo thermal degradation and provide increased pyrolysis yields as heat transfer exceeds mass transfer rates. Leading to higher temperature and cascading into microwave heating of the pyrolysis products that were formed at these high temperatures (Robinson et al., 2021).

4.3.3. The Bio-Oil Extract

Microwave pyrolysis does not allow for simple temperature control and thus may produce more degrading temperatures that may further breakdown pyrolysis products of biomass (such as pyranoses and furans) into water or CO_2 or other lighter bio-oil fractions. A sugar based bio-oil with the charred date pit as a solid residue was expected but given the results of the hydrothermal bio-oil (see 4.2.3), it would not be surprising to see a larger phenolic fraction blended into the extract as higher temperatures are reached. In the hydrothermal microwave experiments, the main aim was to extract lignin/phenolics as a separate solid extract but in practice this was not the case. Seeing as the bio-oil fraction in the hydrothermal experiments, though low in quantity, contained the majority of the extracted phenolics, the hope for this section was to observe the same effect occurring in the dry microwave pyrolysis of the date pits. However, this proved unsuccessful as seen in Table 4.22. Key to note is that upon freeze drying the bio-oils obtained from dry microwave pyrolysis had lost between 75 – 80% of their mass which would be attributed to water or very lightweight volatiles (ethanol, methanol, etc.). That being said it is clear that their phenolic content is very low when compared to the yields obtained from the hydrothermal microwave tests (1 – 14% vs. 29% respectively). There is also a high amount of sugars (furanic and pyranic) indicating a chance for the dry microwave bio-oils to be more successfully fermentable into bio-ethanol than the hydrothermal oils which contain larger variety of materials.

Table 4.22 GC/MS analysis of freeze dried bio-oil extracts obtained from increasing powers and chopped samples, showing an increase of sugar-based content with increasing power.

Group Component	**% Composition from GC/MS**			
	300W	**500W**	**700W**	**Chopped 500W**
Short-chained compounds (> 2C, ≤6C)	7.56	8.75	6.14	7.40
Furans (4C, 1O rings)	42.04	27.9	31.71	51.16
Glucose related compounds) / Pyranoses (5C, 1O rings)	32.72	56.59	52.1	22.29
Aromatics and 6C rings	10.08	3.45	1.08	13.65
- Catechol	**0.75**	**-**	**-**	**6.17**
Long Chained Organic/Fatty Acids (> 8C)	7.6	3.32	8.96	5.50

Further comparison of the chopped and unchopped bio-oils can be found in Table 4.23. Two consistent occurrences have been observed:

- Volatile components such as short chained compounds and sugars are more prevalent in the uncut samples.
- Aromatic components are more prevalent in the chopped samples (although the quantities are still low overall).

This can indicate that less thermal degradation occurs within the chopped date pits due to water escaping and lowering the overall processing temperature internally, with some volatile and liberated lignin is carried through the openings in the date pits. There is also a significantly lower chance for thermal runaway as fewer microwave favourable components are made, such as levoglucosan and furfural due to the presence of aromatics and heavy fatty acids. As well as following the trend of lower overall phenolic content with higher powers, the chopped date pits still consistently have more phenolic content than the unchopped samples backing up the hypothesis that they are not exposed to higher temperatures during processing due to freedom of movement for the water molecules.

Table 4.23 The bio-oils from chopped and unchopped compared to each other and hydrothermal bio-oil using GC/MS and Py-GC/MS.

Group Component	**% Composition from GC/MS**				
	500W	**Chopped 500W**	**600W**	**Chopped 600W**	**180 °C, 60 min HMW**
Short-chained compounds (> 2C, ≤6C)	8.75	7.40	19.17	20.76	17.57
Furans (4C, 1O rings)	27.90	51.16	32.85	34.03	16.53
Glucose related compounds) / Pyranoses (5C, 1O rings)	56.59	22.29	47.98	38.71	20.41
Aromatics and 6C rings	3.45	13.65	0	1.71	29.10
- Catechol	**-**	**6.17**	**-**	**-**	**11.29**
Long Chained Organic/Fatty Acids (>	3.32	5.50	0	4.80	16.18

8C)

Overall, when combining the data and analysis from the date pits and bio-oils the effect the latent moisture content plays in processing biomass in dry microwave conditions can be seen; by triggering the formation of microwave lossy materials and encouraging thermal runaway and fast pyrolysis conditions. Furthermore, the boost that it gives to the production of fermentable bio-oil when using less processed biomass, that is to say biomass that has not been ground and has space to allow the microwaves to propagate between the air pockets to the next portion of biomass. While the “chopped” bio-oils have produced a more phenolic yield of bio-oil, in terms of quantity the whole date pits produced significantly more glucose based bio-oil that can be used to generate a bio-ethanol industrial stream more so than the hydrothermally obtained bio-oils. The lack of phenols in the bio-oils is promising in that they could have either remained slightly degraded or generally whole in the biomass or fully (while unlikely due to their thermal stability) degraded into lighter components that have been dried off in freeze drying. This is fine either way as with further investigation, it can be found if there is a way to generate lighter product fractions in greater quantity from the bio-oil or if a useful solid phenolic source can be exploited.

4.4. Methodology Comparison

To compare the methods used in this thesis is a matter of analysing and comparing the beneficial information and yields obtained. The comparison study will include an examination of the results of the hydrothermally processed date pits and the microwave pyrolysed date pits, as well as comparison of the bio-oils and economic interpretation of the potential yields and benefits presented by both methods.

4.4.1. Energy Input vs. Output Potentials

To compare the energy input of these methods, it is necessary to estimate the energy input of the hydrothermal method. This was difficult to accurately measure as the heating characteristics and profile of water would change rapidly due to microwave heating, however due to the visual logs of the microwave power input, the energy applied to the overall sample can be calculated. With an initial power setting of 850W to heat the vessel as fast as possible, the experiments took ~1.5 minutes to reach required temperature conditions, and with a persistent setting of 15W used to maintain the desired temperature for the required time. So from the lowest condition to the highest, the energy input range was between 81 – 130.5 kJ (150 °C, 5 min and 180 °C, 60 min respectively). Whereas for the dry pyrolysis, the termination conditions were subjective to the visual amount of vapour produced at each level as well as the measured absorbed power dropping to <10% of applied power due to volatiles escaping from the biomass. Therefore, the dry microwave processes did not have pre-set processing times beyond the "Energy Input" experiments. Based on the absorbed power measured by the Sairem 2kW microwave generator, the energy applied directly to the date pits was thus found to lie within the range of 43 – 68 kJ. The absorbed energy range was calculated to be between 20 – 26 kJ, with the 100W trial being an outlier at ~36 kJ, possibly because of the slow rate at which the absorbed energy was dissipated as heat and unable to outpace the mass transfer rate of the moisture, not allowing a high enough temperature to cause charring and thermal runaway.

Based on the presented information, it is clear to see in terms of energy input that dry microwave pyrolysis can pyrolyse the date pits, greatly reduce their mass and provide useful yields with far less effort. With regards to the calorific values of the date pits themselves, the outputs were not significantly different in that the date pits from the hydrothermal processing had their calorific values increased to a maximum of 19 kJ/g, whereas the dry pyrolysis date pits higher heating values were between 20 – 26 kJ/g. This is likely due to the hydrothermal process preserving more cellulose and lignin in the biomass while the dry pyrolysis had charred a significant portion of the date pits. Even though this difference is slight, the dry microwave date pits used far less energy to produce 20 kJ/g of biochar, while making it significantly softer and lighter for transport and mechanical processing.

4.4.2. Products and Benefits

With respect to the extracted yields other than the charred date pits, their quantity and value, they will be compared via examining their overall value generated (assuming optimal condition and purities) financially and as resources. So although the hydrothermally processed date pits provided the least energy bearing char and low amounts of by-products, the main benefit is that this method provided a variety of products. As well as freeing the date pits of low energy lignocellulosic material (hemicellulose mainly), while generally maintaining the mass of the other fractions and simply browning them as an effect of the heat and presence of hemicellulose by-products. This is evidenced by the examination of the DTA results of these pits that show a disappearing hemicellulose peak, the increased height and therefore burning rate of the cellulose peak (due to ease of access) and by their increased caloric values as higher energy components remain. A compact yield of cellulose/sugar ripe for secondary processing that can be used as food supplementary material or bioethanol sourcing.

The same can be said of the bio-oil extracted through dry pyrolysis, containing large fractions of fermentable components in sizable quantities in comparison to the hydrothermal bio-oils. For the dry microwave pyrolysis in all samples; chopped or whole, 100W to 700W, > 70% of the freeze dried bio-oil were furan and glucose related compounds and therefore fermentable into bio-ethanol, while the hydrothermal method produced < 40% of the bio-oil as fermentable by-products. The differences (aside from quantity) can mainly be found in the compositional dissimilarities. Sugar content included, the hydrothermal bio-oil was found to contain more diversity in its contents, as well as significantly higher phenolic content, making it a viable fuel additive source as opposed to a strictly fermentable bio-ethanol source like the dry pyrolysis bio-oil. This is also keeping in mind that the dry pyrolysis oil contains ~80 % of its yield as light volatiles and moisture (measured through drying and weighing), thus showing the dry pyrolysis oil and hydrothermal oils were roughly similar in quantity (6.29 % and 6.3 % at maximum conditions respectively). The overall outcomes are illustrated Figure 4.32 below.

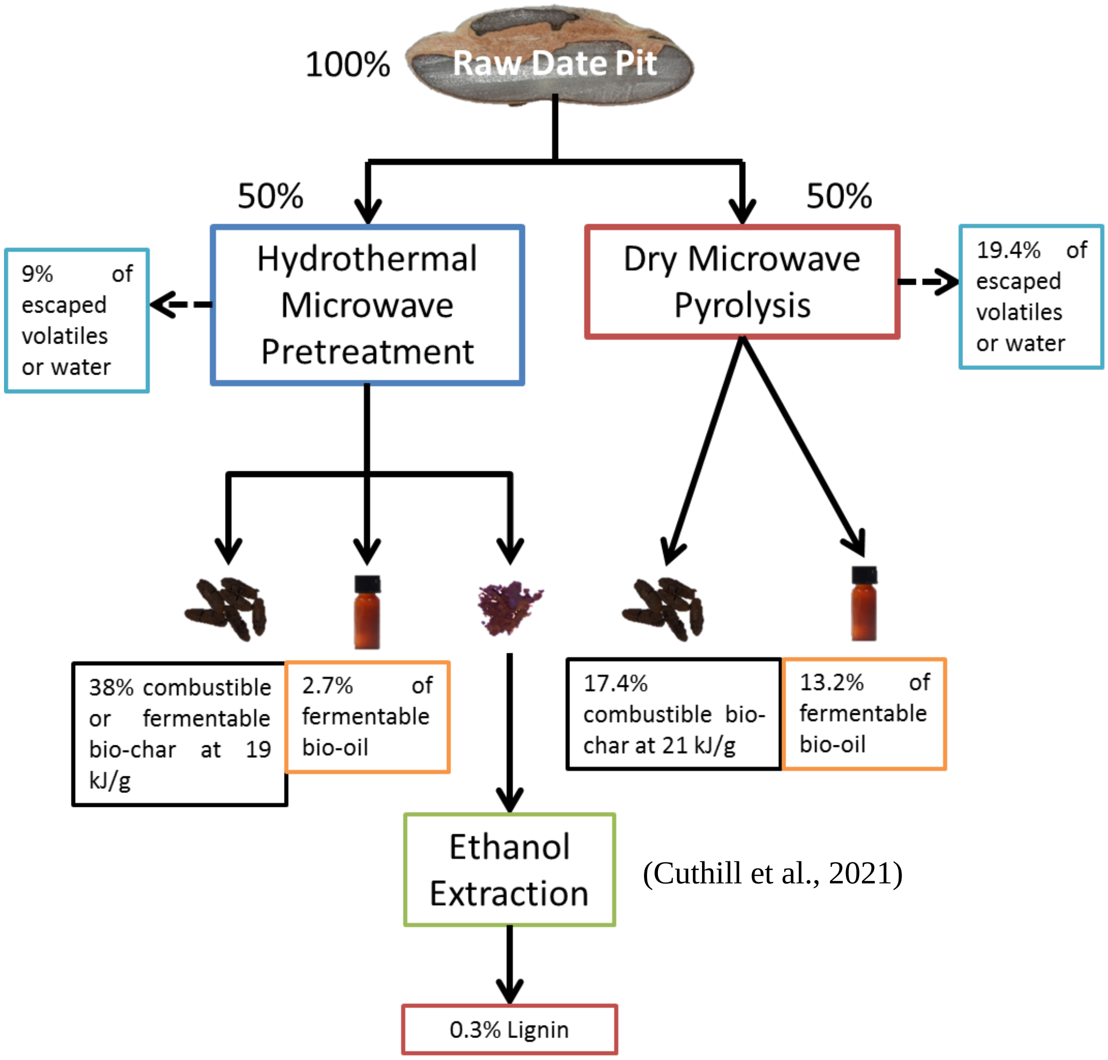

Figure 4.32 The balanced outcomes of both methods, using the maximum conditions as a basis (180 °C and 60 mins for Hydro MW and 700W for Dry MW)

To fully grasp the potential of the dry pyrolysis bio-oil as a bio-ethanol source, several hypotheses and assumptions should be made to build a comparative estimate:

- A hypothetical combination of known hydrolysis and fermentation techniques (Bennett et al., 2009; Binder & Raines, 2010; Geng et al., 2012; Fang et al., 2015; Fang et al., 2015; Goswami et al., 2015) would be used to maximise the potential bio-ethanol production efficient to 90 % (As in 90 % of input glucose is to be converted to bio-ethanol under ideal conditions).

- Though some of the sugars found in the GC/MS of the bio-oils contain multiple glucose molecules, most of the glucose related compounds contain at least one molecule and will be considered as such for the sake of production estimates.
- Furans do not contribute heavily to bio-ethanol production and will not be considered for estimation quantities.

The following expectations are generated by coupling the above assumptions with the obtained glucose quantities in the bio-oil extracts of both methodologies (20.4 % in the hydrothermal bio-oil and 56.6% in the 500W dry microwave bio-oil) keeping in mind their respective overall yields. With these assumptions in mind, and at 2 ethanol molecular units produced per glucose unit, it can be estimated that the bio-ethanol productions from the respective bio-oils from just the glucose fractions are as such:

- For every 100 grams of hydrothermally processed date pits:
  - 22.29 g of glucose related compounds would be produced (or 0.123 moles of glucose).
  - 90 % of the glucose compounds would produce 0.223 moles of ethanol.
  - Total estimated theoretical yield of bio-ethanol = 10.3 g of ethanol / 100 g of date pits.
- For every 100 grams of dry microwave pyrolysis date pits at 500W (maximum glucose/pyranoses yield):
  - 56.59 g of glucose related compounds would be produced (or 0.314 moles of glucose).
  - 90 % of the glucose compounds would produce 0.565 moles of ethanol.
  - Total estimated theoretical yield of bio-ethanol = 26.0 g of ethanol / 100 g of date pits.

So the dry pyrolysis date pits are potentially capable of producing more than twice the amount of bio-ethanol from the bio-oil extract than the hydrothermal method. Bio-ethanol has a higher heating value of 29.8 MJ/kg and has value in the refineries of the Sultanate of Oman as a potential liquefied natural gas (55.2 MJ/kg) and liquefied petroleum gas (50.2 MJ/kg) renewable substitute or supplement. The price to sell bio-ethanol is averaged at £2.50 per litre at current pricing, but this methodology may introduce a way to reduce prices and make renewable fuels more attractive to refineries and consumers.

Finally, the solid extracts can be examined for the potential benefits obtained from each method. While both ways succeeded in softening the date pits for mechanical processing or as a softer food for animal feeds, each method treated the date pits differently, providing vastly different uses post-processing. For example, the dry microwave pyrolysed date pits' inherent heating values increased slightly more than the hydrothermally processed date pits. This shows that they have also charred more and are likely unfit for animal consumption (though animals like humans can eat cooked if not burnt food), but they are suitable to be used as a clean and renewable coal/charcoal substitute. The hydrothermal date pits had been preserved better in the sense that although the lignocellulosic structure has crumbled and been opened, they can provide a good source of sugars and phenolics that can be acquired through secondary processing methods. These preserved components can be used as beneficial and high value platform chemicals for various downstream industries. Speaking of phenolics, another benefit to the hydrothermal method is that it can separate the lignin fraction from the date pit itself (even though it is a low quantity) as a powder with a high concentration of phenolics. With more work, better yields can be obtained to be used as a viable income stream based on this method. Considering the price for lignins increase with purity and chain lengths, there is a benefit to not using destructive chemicals and methods to extract this fraction. There is also the fact that although most of the lignin fraction was not extracted from the date pits, they remain generally preserved in the date pit residue and are easier to separate from the degraded cellulosic chains.

5. Conclusions

Date pit characterisation has shown, for the first time that the two distinct layers (the skin and the core) have vastly different compositions which are the skin having more lignin than the core (>27% versus <10% respectively) and the core consisting mainly of cellulose/starch.

Based on the characterisation of the raw date pits, it is evident that there is a reliable source of phenolics or cellulose and sugars contained within. It is also clear that the phenolics and sugars are clearly and naturally separated, thus eliminating the need for a mechanical grinding process that would mix the components unnecessarily. This leads to a need for a process that would separate the skin from the core reliably and non-destructively in a general sense in that, it would maintain the composition of the phenolics and sugars while also being an environmentally friendly and relatively economical method.

Microwave processing was suggested as a potential method; however the dielectric analysis has shown that the date pit biomass components are relatively microwave transparent. It should be noted though that these measurements were taken under slow pyrolysis and unpressurised conditions. Thus, the small peaks that appear below water boiling point and within hemicellulose degradation temperature range suggest two assumptions:

1. As low as the moisture content is in date pits, the moisture still plays an important role in activating the dielectric effects within the biomass
2. The products of hemicellulose degradation promote microwave heating at higher temperatures, and heating is more effective if they are able to remain contained in the biomass.

Two methods were proposed to adhere to the economical and environmentally benign expectations of the thesis: hydrothermal microwave extraction (HME) and dry microwave fast pyrolysis. These were suggested also with regards to the Sultanate of Oman’s natural environment of extremely dry or efficiently desalinated water taken from the sea. Though obvious, it should be stated that these methods had common and unique advantages to each other. These advantages can be utilised depending on the processing environments and desired end products. A comparison is drawn in Table 5.1 below to outline the benefits, drawbacks and main yields of the methods.

Table 5.1 A comparison of the methodologies and their outcomes.

	Benefits	Drawbacks	Yields
Hydrothermal Microwave Extraction	• Relatively quick and environmentally friendly pre-treatment method. Also enabling environmentally benign pre-treatment. • Good temperature control with water acting as medium and quencher. Preventing thermal runaway.	• Low extractive yields. • Relatively large amount of water used for low yields. • Lab-scale safety concerns resulting from pressure conditions.	• Sugar-rich and soft date pit husk/bio-char. • Phenolic rich solid extract. • Diverse bio-oil.
Dry Microwave Pyrolysis	• Extremely rapid method. • Direct treatment and energy transfer into biomass. • Direct observation of microwave effects.	• Difficult temperature control, chance of thermal runaway. • Biomass may not be receptive to microwave radiation.	• Light and soft bio-char. • Light sugary bio-oil.

With regards to the products obtained from both methods, while the dry pyrolysis method provides a higher amount of bio-oil, the hydrothermal method produces more variation of products overall as well as in the bio-oil extracts. The hydrothermal method had extracted more of the phenolic content as both solid residue and as a fraction of the bio-oil residue, had more been obtained it would encourage using fractional distillation or precipitation methods to separate the phenolic fraction from the bio-oil. Whereas the dry microwave bio-oil was greater in quantity, it was also contaminated with a significant water fraction from the moisture and breakdown of hemicellulose and light pyrolysis products (due to thermal runaway and high temperatures). It was also less variable in its composition, which means less post-processing to separate the sugar by-products and a bio-oil that is more prepared for bio-ethanol production.

In terms of date pits post-processing, both methods had significantly softened the date pits (from 1.5 – 2.0 kN crushing force down to < 0.5 kN) and upgraded their energy potentials by carbonising weaker components and maintaining the thermally stable components. The main difference being that the hydrothermal method preserved the cellulose and lignin fractions more fully, while it is unclear how preserved these fractions are in the dry microwave pyrolysed date pits. The lignins in the dry microwaved date pits must have been preserved as very few phenolic by-products had been collected in the bio-oil residue when analysed via GC/MS, and it is unlikely they would vaporise quickly due to their thermal stability seen in TGA.

The dry microwave method also highlighted several key behaviours that were instrumental in determining the effect of microwave radiation on date pit biomass:

- When testing the effect of applied power, the bio-oil yields increased with increasing power and at exponentially faster rates. The energy absorbed at the variable rates was also similar and this lead to testing the effect of controlled energy input. This is an indication that the process is power density driven; potentially increasing bio-oil yields and reducing power requirements in industrial scale processes.
- The effect of sample preparation was investigated; to see whether pre-grinding or chopping the date pits would be a beneficial pre-processing step. It was seen that when the biomass was pre-chopped, the overall energy absorption decreased throughout the sample. This was caused by the ability of internal moisture to evaporate from the date pits without leading to superheating and the associated microwave heating of degradation products such as levoglucosan seen during the pyrolysis of whole date pits. The tighter packing in the reactor also resulted in lower penetration depths into the biomass. This led to incomplete heating of the date pit biomass. This result shows that microwave processing of whole date pits is inherently better than pre-chopped pits. This finding could have major implications to the capital and operating costs of microwave pyrolysis compared with conventional pyrolysis, which would require an extra high energy intensity unit operation (size reduction).

- When testing the effect of controlled energy input, while this is generally difficult to perform due to the variable microwave absorptivity of the biomass, the results show that the amount of energy is important in generating optimal yields at lower powers while the energy transfer rate (controlled by the input power and dielectric loss tangent of the material) plays a more significant role at higher powers with some contribution from the absorbed power.

Overall, if the aim was to obtain a variety of products, hydrothermal processing is an environmentally benign method that may require more development and optimisation to increase yields. If the aim was to quickly soften the dates and obtain a liquid residual by-product, dry microwave pyrolysis is the superior method without obtaining a solid phenolic extract since it has a lower energy requirement, heating the biomass without wasting energy to heat water. Both methods increase the calorific output of the date pits, but the dry microwave pyrolysis produces a more fermentable bio-oil that can be converted into high energy bio-ethanol.

To conclude with the answer to the question at the start of this study, can date pits replace crude oil? Yes, but not yet and not through traditional means. This study has managed to make several contributions in the field of microwave processing of date pit biomass in that: the distribution of lignin content was identified and the date pits were softened while preserving said lignin and sugar contents. The main drawback being that far less lignin residues were produced and may require more steps to produce and refine. While the energy of bio-ethanol is good and clean, it still combusts to provide less energy than regular petroleum and natural gas which the Sultanate of Oman heavily relies on. The hardness of date pits is one of the major challenges that would need to be overcome. While conventional thermal methods may be able to generate processable date pits, the application of microwave energy is also another hurdle that would need to be overcome. This thesis does present however the alternative that the if hardest biomass can be processed to be valorised as a platform chemical source and a bio-fuel source, then so can softer waste material that would otherwise arrive at a landfill and present no further value.

6. Future Work

Due to the COVID-19 pandemic impeding physical work, several items in this section were meant to be pursued but hopefully will be carried out at a later time under better circumstances. The following suggestions are provided in hopes that future researchers carry out some of the studies to maximise the potential of microwave processing and date pit biomass valorisation.

- Improving the volatiles capturing step of the dry microwave pyrolysis methodology to expand the bio-oil generation aspect of this experiment and improve yields and value.
- The obtained bio-oil from the dry microwave pyrolysis can be fractionally distilled and converted into bio-fuels, to accurately grasp the potential for date pits to replace fuels as a bio-ethanol or bio-diesel source. This would have to be done shortly after extraction as, due to the sugar fraction in the bio-oil and significant water contamination, the bio-oil is highly susceptible to fungal growth and contamination.
- Optimising production and conversion of the phenolic extracts into viable products that can feed into the plastics, fuel additives and other related industries.
- Development of reliable lignin estimation techniques and addition of useful information to existing data, in case of unsatisfactory laboratory condition or other hindering circumstances (such as a pandemic) rendered the researcher incapable of using relevant facilities.
- Observe and test the potential uses of the bio-char/processed date pits which include based on previous studies:
    - Viability as an animal feed or as human safe food additive.
    - Viability as a solid fuel source.
    - Sugar (cellulose) and phenolic rich platform chemical source.
    - Use as an activated carbon pellet or powder now that it has been significantly softened via microwave processing.

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Appendices

A. Proximate Analysis Data of Hydrothermally Processed Date Pits

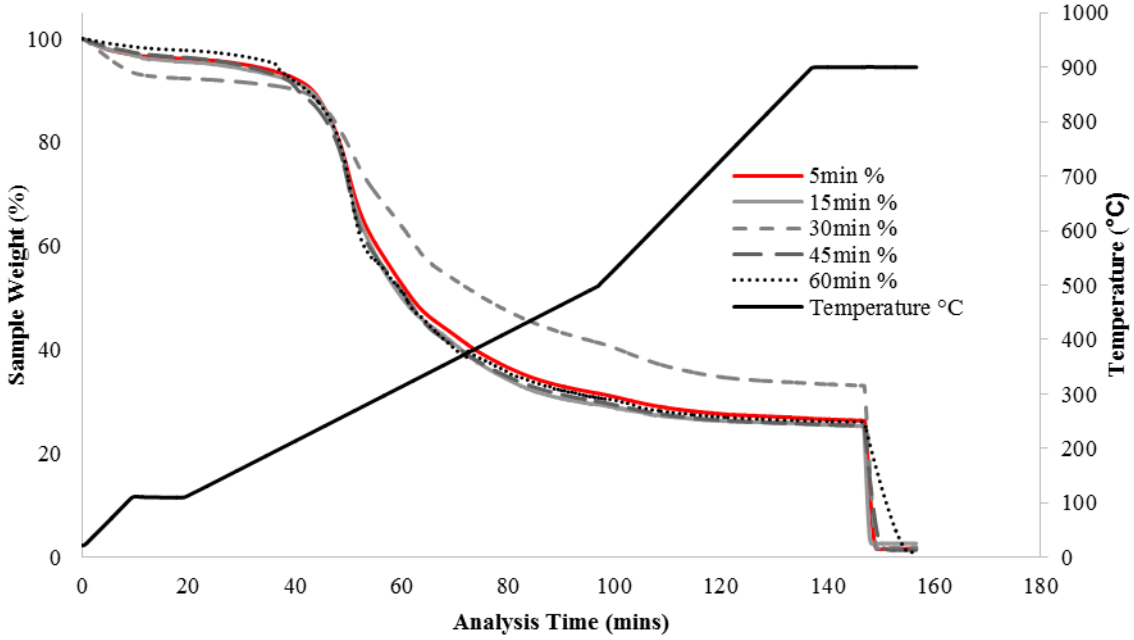


Figure 0.1 TGA data of date pits processed at 150 °C, including temperature ramp profile.

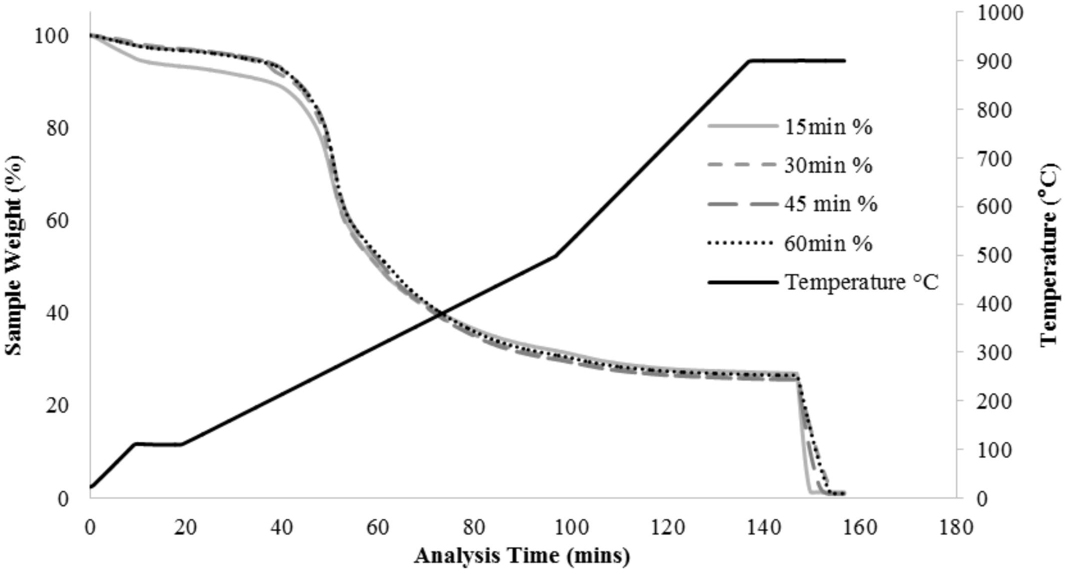


Figure 0.2 TGA data of date pits processed at 160 °C, including temperature ramp profile.

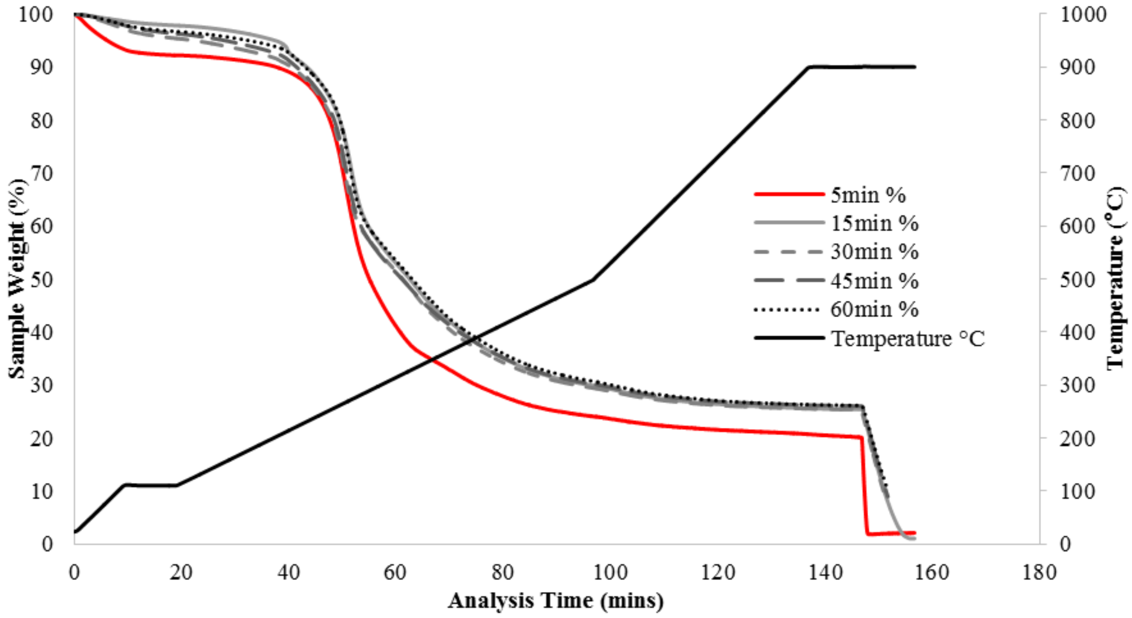


Figure 0.3 TGA data of date pits processed at 170 °C, including temperature ramp profile.

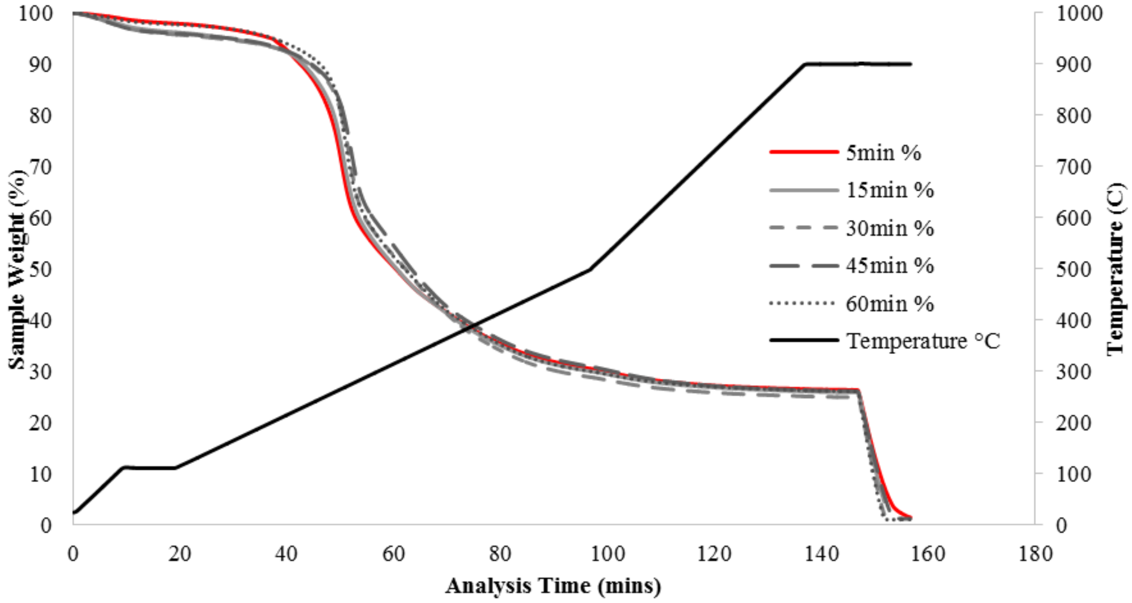


Figure A.4 TGA data of date pits processed at 180 °C, including temperature ramp profile.

B. GC/MS Data

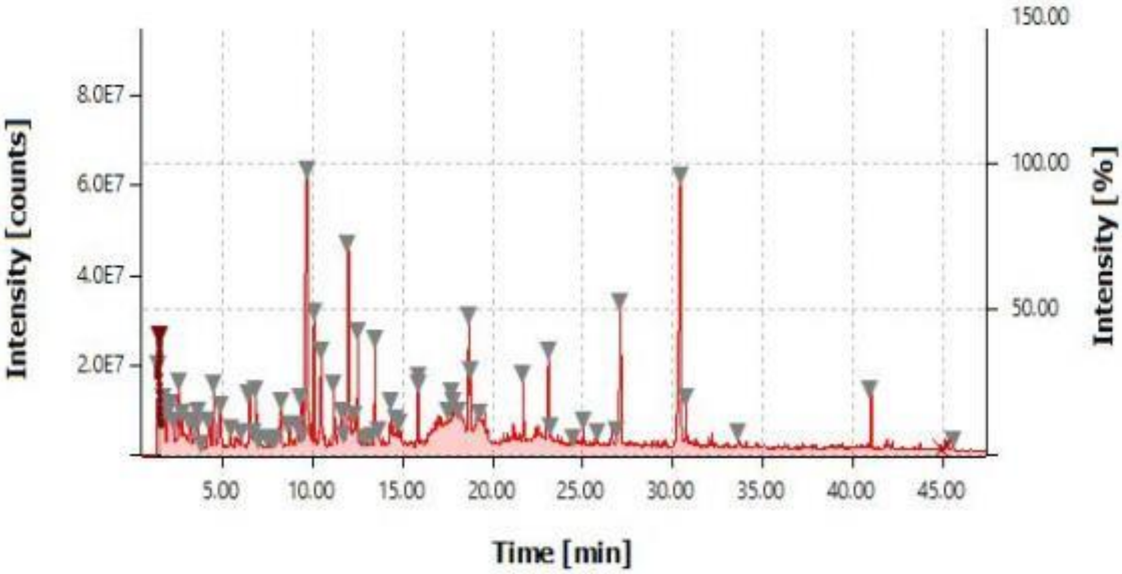


Figure B.5 The chromatographs of date pit skin (DPS).

Table B.1 The identified peaks for the pyro-chromatographs of date pit skin (DPS).

Peak	RT	Compound	Peak Area %
1	1.404	1-Butanol, 2-amino-	1.75
2	1.49	Pentanoic acid, 3-methyl	7.20
3	1.679	Propanoic acid	1.35
4	1.793	Cyclohexene-3,5-diol, cis-	0.19
5	1.988	1,5-Heptadiene	1.67
6	2.102	Benzeneacetic acid, heptyl ester	1.09
7	2.268	Tetrahydro-4H-pyran-4-ol	1.04
8	2.565	2,4-Dimethylfuran	2.85
9	2.743	2-Furanmethanol	0.84
10	3.201	Hexanoic acid, 2-phenylethyl ester	0.56
11	3.512	2H-Pyran, 3,4-dihydro-	1.25
12	3.63	Cyclohexanone	1.71
13	3.887	9-Decenoic acid	0.15
14	4.259	Cyclohexanol, 2,3-dimethyl-	0.79
15	4.519	Phenol	3.43
16	4.883	2H-Pyran-2-methanol, 6-ethoxy-3,6-dihydro-3-hydroxy-	1.73
17	5.455	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.63
18	6.027	Phenol, 3-methyl-	0.23
19	6.491	p-Cresol	1.70
20	6.702	2-Furancarboxylic acid, 2,2-dimethylpropyl ester	0.58
21	6.846	Phenol, 2-methoxy-	1.77
22	7.069	Undecanal	0.55

23	7.761	2-Hydroxy-6-methyl-3-cyclohexen-1-carboxylic acid	0.17
24	7.967	Cyclopentane, (3-methylbutylidene)-	0.79
25	8.259	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	1.79
26	8.705	Phenol, 2-ethyl-	0.96
27	9.157	Melezitose	0.75
28	9.38	Creosol	0.51
29	9.472	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.14
30	9.644	Catechol	10.10
31	10.074	Benzofuran, 2,3-dihydro-	4.00
32	10.519	5-Hydroxymethylfurfural	5.17
33	11.183	1,2-Benzenediol, 3-methyl-	1.46
34	11.463	Melezitose	0.60
35	11.606	Phenol, 4-ethyl-2-methoxy-	0.70
36	11.732	Cyclohexanol, 2,2-dimethyl-	0.42
37	11.974	1,2-Benzenediol, 4-methyl-	7.88
38	12.344	2-Hexadecenoic acid, methyl ester, (E)-	0.40
39	12.505	2-Methoxy-4-vinylphenol	2.29
40	12.985	l-Gala-l-ido-octose	0.22
41	13.26	Benzoic acid, 4-(1,1-dimethylethoxy)-	0.16
42	13.472	Phenol, 2,6-dimethoxy-	2.03
43	13.529	1,4-Benzenediol, 2,5-dimethyl-	0.18
44	13.666	2,4-Dimethoxyphenol	0.19
45	14.342	4-Ethylcatechol	1.71
46	14.845	Cinnamic acid	0.15
47	15.846	Phenol, 4-methoxy-3-(methoxymethyl)-	0.98
48	15.886	Phenol, 2-methoxy-4-(1-propenyl)-	0.65
49	17.563	D-Allose	0.46
50	17.889	D-Allose	1.14
51	17.941	D-Allose	0.24
52	18.089	D-Allose	1.15
53	18.667	3-tert-Butyl-4-hydroxyanisole	1.51
54	18.787	Dodecanoic acid	0.83
55	19.285	Melezitose	0.57
56	21.7	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (Sinapyl)	0.96
57	23.102	Tetradecanoic acid	1.54
58	23.239	trans-Sinapyl alcohol	0.35
59	24.458	9,10-Secocholesta-5,7,10(19)-triene-3,24,25-triol	0.40
60	25.042	Oleic Acid	0.21
61	25.826	Oleic Acid	0.21
62	26.924	Oleic Acid	0.16
63	27.113	n-Hexadecanoic acid	2.15
64	30.409	Oleic Acid	4.98
65	30.752	Oleic Acid	0.25
66	33.613	Oleic Acid	0.20

67	41.006	Squalene	1.24
68	45.578	Oleic acid, 3-(octadecyloxy)propyl ester	0.15

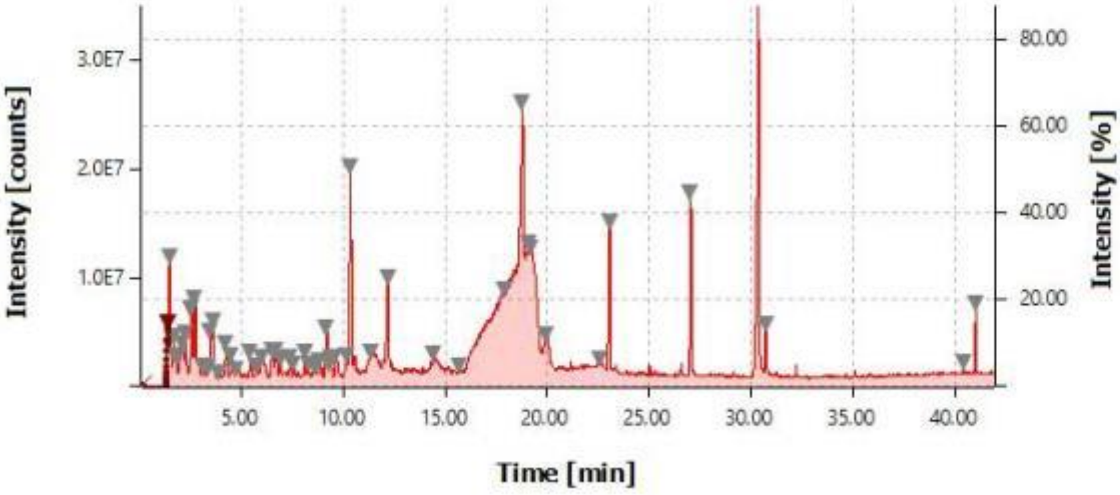


Figure 0.6 The chromatographs of date pit core (DPC).

Table 0.2 The identified peaks for the pyro-chromatographs of date pit core (DPC).

Peak	RT	Compound	Peak Area %
1	1.404	2-Butanamine, 2-methyl-	1.35
2	1.484	Pentanoic acid, 3-methyl-	8.10
3	1.661	Hexanoic acid, 2-methyl-	2.33
4	1.787	Cyclohexanol, 2-methyl-, cis-	0.44
5	1.919	2-Pentene, 4-methyl-	0.33
6	1.993	1-Cyclohexyl-2-propen-1-ol	0.78
7	2.153	1,3-Dioxane-2-propanol, 2-methyl-	1.51
8	2.273	Furan, 2,3-dihydro-5-methyl-	3.27
9	2.565	Furan, 2,5-dimethyl-	4.00
10	2.743	2-Furanmethanol	3.25
11	3.149	L-Glucose	0.23
12	3.355	4,4-Dimethyl-non-5-enal	0.52
13	3.498	2(5H)-Furanone	3.05
14	3.618	1,2-Cyclopentanedione	3.30
15	3.904	Hex-3-ene-1,6-diol	0.37
16	4.259	Furfural, 5-methyl-	1.57
17	4.516	9-Decenoic acid	0.43
18	4.722	1,6-Anhydro-2,4-dideoxy-β-D-ribo-hexopyranose	0.22

19	5.443	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.07
20	5.712	Cyclohexanone, 2-(hydroxymethyl)-	0.16
21	5.77	3(2H)-Furanone, dihydro-5-isopropyl-	0.36
22	6.027	2(3H)-Furanone, 5-heptyldihydro-	3.51
23	6.502	2,2-Dimethyl-3-vinyl-bicyclo[2.2.1]heptane	0.28
24	6.559	3,6-Dimethyl-5-hepten-1-ol acetate	0.41
25	6.697	2-(Hydroxyacetyl)furan	2.10
26	6.92	cis-2,2-Dimethyl-4-Decene	1.68
27	7.378	Maltol	0.79
28	7.578	2H-Pyran-3(4H)-one, dihydro-6-methyl-	0.45
29	8.133	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	0.77
30	8.282	2(3H)-Furanone, 5-heptyldihydro-	0.35
31	8.619	Benzoic acid, 4-(1,1-dimethylethoxy)-	0.42
32	8.86	Benzoic acid	0.47
33	9.22	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	2.30
34	9.329	2(3H)-Furanone, 5-heptyldihydro-	1.00
35	9.415	1,4:3,6-Dianhydro-α-d-glucopyranose	0.80
36	9.615	Catechol	1.68
37	10.181	Maltose	0.63
38	10.393	5-Hydroxymethylfurfural	12.88
39	11.377	Cyclohexanol, 2,2-dimethyl-	1.73
40	12.195	Melezitose	2.88
41	13.552	Melezitose	0.14
42	14.479	Melezitose	1.42
43	15.68	Melezitose	0.13
44	17.734	D-Allose	0.35
45	18.799	D-Allose	4.34
46	19.113	D-Allose	0.37
47	19.222	D-Allose	2.96
48	19.977	Melezitose	2.47
49	22.587	Melezitose	0.69
50	23.067	Tetradecanoic acid	2.80
51	27.044	n-Hexadecanoic acid	2.80
52	30.352	Oleic Acid	7.53
53	30.712	Oleic Acid	0.36
54	40.417	Octadecanedioic acid	0.16
55	41	Squalene	1.74

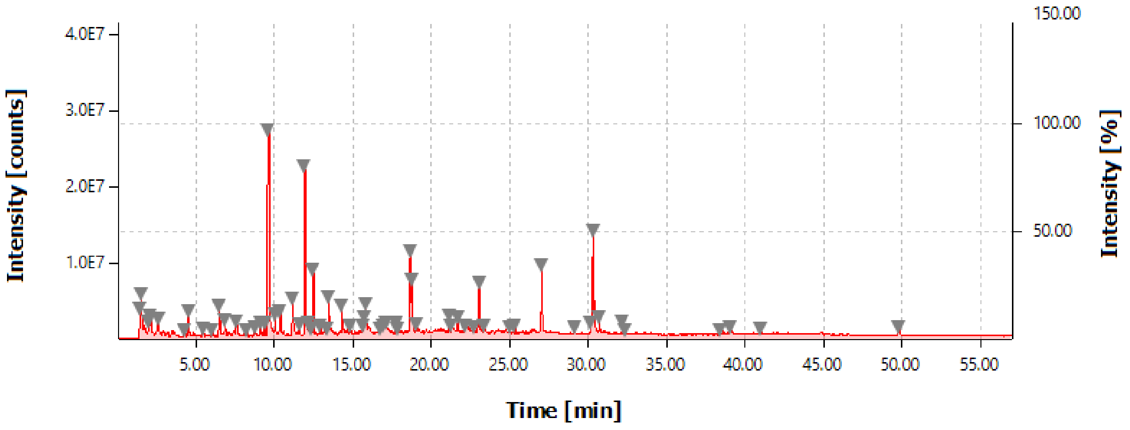


Figure 0.7 The chromatograph of the phenolic rich Solid Extract/Powder from the hydrothermal processed date pits (180 °C for 60 mins).

Table 0.3 The identified peaks of the phenolic rich Solid extract/powder from the hydrothermal processed date pits (180 °C for 60 mins).

Peak	RT	Compound	Peak Area %
1	1.409	2-Butanamine, 2-methyl-	0.88
2	1.49	Acetic Acid	1.55
3	1.535	Acetic Acid	0.95
4	1.678	Pentanoic acid, 4-methyl-	0.45
5	1.993	Toluene	0.70
6	2.108	Toluene	1.22
7	2.582	Furan, 2,5-dimethyl-	1.05
8	2.874	Styrene	0.38
9	3.475	Cyclohexanol, 2,3-dimethyl-	0.41
10	3.607	Cyclooctanone, 2-methyl-	0.36
11	4.265	Furfural, 5-methyl-	0.45
12	4.517	Phenol	1.66
13	5.432	Cyclohexanone, 3-methyl-, (R)-	0.63
14	6.033	Phenol, 3-methyl	0.51
15	6.468	Phenol, 4-methyl-	1.89
16	6.834	Guaiacol	0.84
17	7.372	1,3,5-Benzenetriol	0.32
18	7.543	Catechol carbonate	1.10
19	7.664	3-Pyridinol	0.47
20	8.242	2,3-Xylenol	0.27
21	8.751	2,5-Xylenol	0.61
22	9.088	Phenol, 4-amino-	0.55
23	9.38	Creosol	0.43
24	9.632	Catechol	26.81
25	10.044	Coumaran	0.60
26	10.364	Resorcinol monoacetate	1.47

27	11.143	1,2-Benzenediol, 3-methyl-	2.53
28	11.595	p-Ethylguaiacol	0.42
29	11.927	4-Methylcatechol	10.86
30	12.127	Salicin	0.33
31	12.482	4-Vinylguaiacol	2.29
32	13.437	Syringol	1.36
33	13.512	1,4-Benzenediol, 2,5-dimethyl-	0.99
34	13.637	Benzenemethanol, 3-hydroxy-5-methoxy-	0.28
35	14.29	1,2-Benzenediol, 4-ethyl-	1.86
36	14.627	Vanillin lactoside	0.33
37	14.828	2-Methyl-5-hydroxybenzofuran	0.38
38	15.64	Melezitose	0.29
39	15.749	(3-Nitrophenyl) methanol, 3-methylbutyl ether	0.63
40	15.818	Phenol, 4-methoxy-3-(methoxymethyl)-	1.83
41	16.035	2-Propyn-1-ol,3-(4-methylphenyl)	0.41
42	16.985	Melezitose	0.29
43	17.099	Melezitose	0.29
44	17.734	5-Tert-Butylpyrogallol	0.35
45	18.639	3-tert-butyl-4-hydroxyanisole	3.57
46	18.759	Dodecanoic acid	3.84
47	19.045	2-Propenoic acid, 3-phenyl-	0.49
48	21.15	1-Hexadecanol, 2-methyl-	0.62
49	21.677	4-Allylsyringol	0.59
50	22.209	Papaveroline, 1,2,3,4-tetrahydro-3-O-methyl-	0.65
51	22.386	Benzaldehyde, 2,3,4-trimethoxy-	0.29
52	23.044	Tetradecanoic acid	2.86
53	23.313	Salsoline	0.33
54	24.177	Salsoline	0.29
55	24.732	2-(7-Hydroxymethyl-3,11-dimethyl-dodeca-2,6,10-trienyl)-[1,4]benzoquinone	0.34
56	24.996	Benzoic acid, 2,3-dimethyl-6-(3-methyl-1-oxobutyl)-	0.29
57	27.05	n-Hexadecanoic acid	3.82
58	30.317	Oleic Acid	6.53
59	30.392	Oleic Acid	1.16
60	30.695	Oleic Acid	0.61
61	32.188	9-Hexadecenoic acid	0.43
62	39.043	Oleic acid, eicosyl ester	0.36
63	49.824	β-Sitosterol	0.67

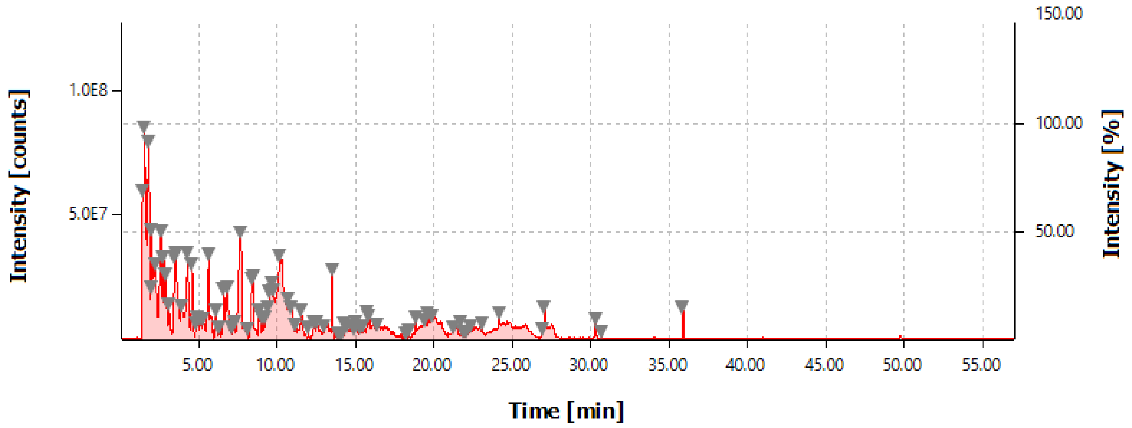


Figure 0.8 The chromatograph of the hydrothermal date pits bio-oil, after freeze drying.

Table 0.4 The identified peaks of the hydrothermal date pits bio-oil, after freeze drying.

Peak	RT	Compound	Peak Area %
1	1.591	Acetic acid	14.03
2	1.854	4-Penten-1-ol, 2,2,4-trimethyl-	0.98
3	1.947	1-Methoxymethoxy-hexa-2,4-diene	0.30
4	2.005	6-Nonynoic acid	1.62
5	2.087	Toluene	1.98
6	2.163	Cyclohexan-1,4,5-triol-3-one-1-carboxylic acid	1.08
7	2.227	Cyclohexan-1,4,5-triol-3-one-1-carboxylic acid	0.54
8	2.262	1,2-cis-1,5-trans-2,5-dihydroxy-4-methyl-1-(1-hydroxy-1-isopropyl)cyclohex-3-ene	0.90
9	2.32	1,2-cis-1,5-trans-2,5-dihydroxy-4-methyl-1-(1-hydroxy-1-isopropyl)cyclohex-3-ene	0.73
10	2.448	Pyridine, 4-methyl-	0.70
11	2.571	Furan, 2,5-dimethyl-	3.54
12	2.757	2-Furanmethanol	1.57
13	2.856	l-Gala-l-ido-octose	0.65
14	2.88	(+)-4-Carene	0.85
15	3.101	Cyclohexene-3,5-diol, cis-	0.66
16	3.444	1-Pentanone, 1-(3-furanyl)-4-hydroxy-	2.34
17	3.551	Propanoic acid, 2-[(tetrahydro-2H-pyran-2-yl)oxy]-	4.38
18	4.034	2-Heptanol	6.98
19	4.269	2-Furancarboxaldehyde, 5-methyl-	2.31
20	4.582	Phenol	3.62
21	4.914	9-Oxa-bicyclo[3.3.1]nonane-1,4-diol	0.29
22	5.13	l-Gala-l-ido-octose	0.45
23	5.269	Paromomycin	0.28
24	5.637	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	2.26
25	5.677	Paromomycin	0.38
26	5.788	Cyclohexanone, 2-(hydroxymethyl)-	0.27

27	5.899	5-Hepten-2-ol, 6-methyl-	0.16
28	6.08	3-O-Benzyl-D-glucose	0.40
29	6.587	Phenol, 3-methyl-	1.19
30	6.756	3-t-Butyl-6-methyl-2H-pyran	1.16
31	6.808	Furaneol	0.31
32	6.866	p-Guaiacol	0.51
33	7.624	Maltol	6.33
34	8.487	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	2.22
35	8.831	2(5H)-Furanone, 4-methyl-3-(2-methyl-2-propenyl)-	0.19
36	9.653	2-Furancarboxylic acid, 1-cyclopentylethyl ester	6.46
37	9.717	5,7-Octadien-3-ol, 2,4,4,7-tetramethyl-, (E)-	3.56
38	10.212	Catechol	9.49
39	10.539	Catechol	1.80
40	10.719	Phenol, 4-ethoxy	0.87
41	10.912	3-Pyridinol, 6-methyl-	1.93
42	11.524	3,4-Dimethyoxytoluene	0.29
43	11.984	Paromomycin	0.20
44	13.5	Syringol	0.93
45	14.31	Cyclohexene, 1,5,5-trimethyl-6-acetylmethyl	0.20
46	14.823	l-Gala-l-ido-octose	0.35
47	15.021	Cyclopropa[d]naphthalen-3-one, octahydro-2,4a,8,8-tetramethyl-, oxime	0.20
48	15.067	Cyclopropa[d]naphthalen-3-one, octahydro-2,4a,8,8-tetramethyl-, oxime	0.25
49	15.854	Paromomycin	0.19
50	16.023	Paromomycin	0.33
51	18.833	Stevioside	0.16
52	20.051	Stevioside	1.37
53	20.15	Melezitose	0.95
54	22.301	2,2-Dimethyl-6-methylene-1-[3,5-dihydroxy-1-pentenyl]cyclohexan-1-perhydrol	0.16
55	24.871	Digitoxin	0.59
56	25.087	Digitoxin	0.42
57	27.069	Dodecanoic acid, 3-hydroxy-	1.32
58	27.314	Actinomycin C2	0.50
59	27.553	Actinomycin C2	0.91
60	35.876	Hexanoic acid, 2-ethyl-, oxybis(2,1-ethanediyloxy-2,1-ethanediyl) ester	0.39

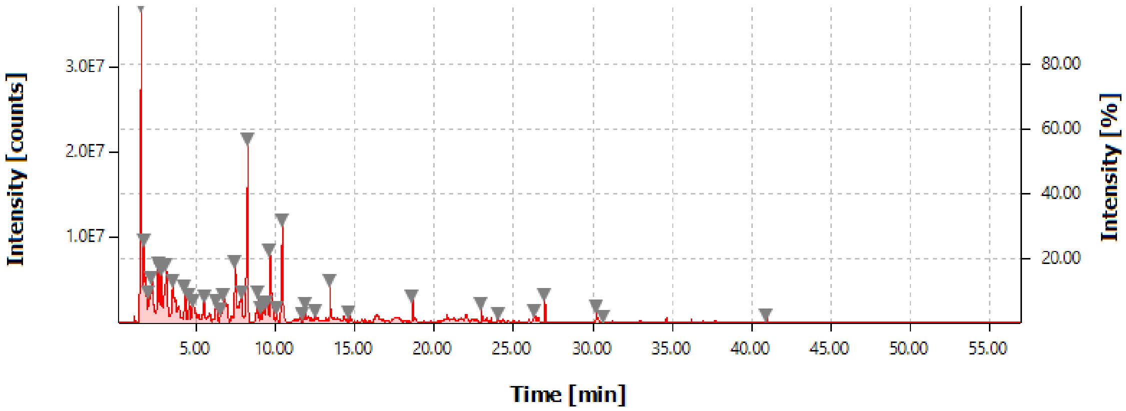


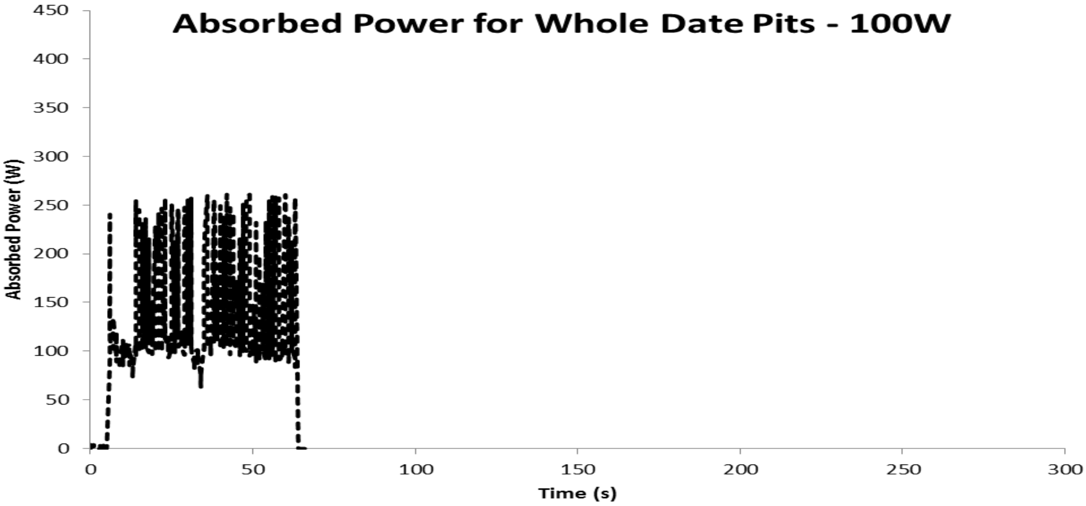
Figure 0.9 The chromatograph of the hydrothermal date pits bio-oil, after oven drying.

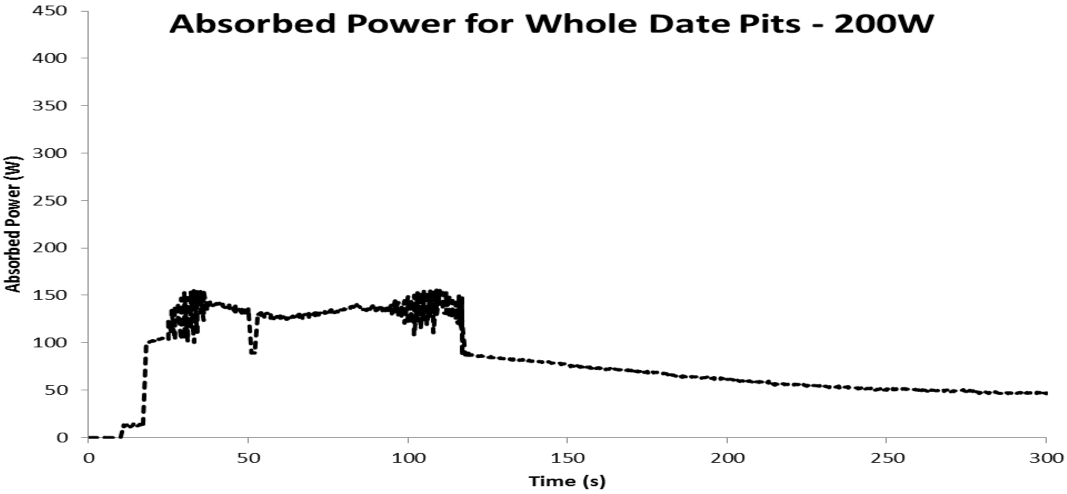
Table 0.5 The identified peaks of the hydrothermal date pits bio-oil, after oven drying.

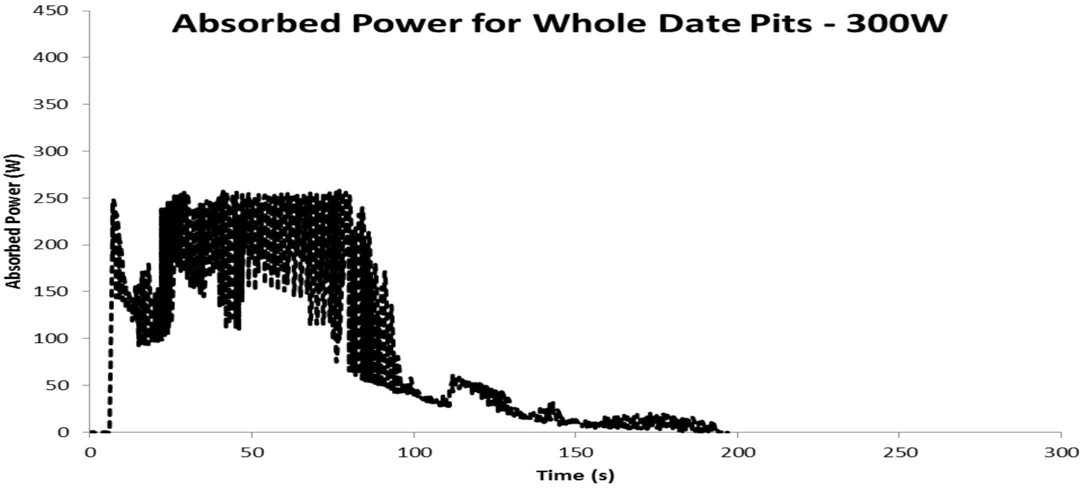
Peak	RT	Compound	Peak Area %
1	1.09	Carbon dioxide	0.29
2	1.416	Acetic acid	4.60
3	1.498	Acetic acid	14.70
4	1.667	2-Propanone, 1-hydroxy-	5.44
5	2.18	2-Butanol, 3-methyl-	2.90
6	2.571	Furfural	2.91
7	2.745	2-Furanmethanol	1.30
8	3.066	L-Lactic acid	10.65
9	3.153	4-Penten-2-oL	2.64
10	3.515	2-Hexene	1.12
11	3.835	Propanoic acid, 3-hydroxy-	0.39
12	4.261	2-Furancarboxaldehyde, 5-methyl-	1.60
13	4.517	Phenyl-β-D-glucoside	1.10
14	4.762	1,6-Anhydro-2,4-dideoxy-β-D-ribo-hexopyranose	0.96
15	5.467	1,2-Cyclopentanedione, 3-methyl-	0.35
16	5.823	3-Acetoxydodecane	0.90
17	6.248	Furaneol	1.94
18	6.552	Orcinol, monoacetate	0.29
19	6.686	2-Furancarboxylic acid, 2,2-dimethylpropyl ester	1.87
20	6.919	2-Furancarboxylic acid, pentadecyl ester	0.63
21	7.432	Maltol	3.43
22	7.863	6-Methyl-2-heptyne	6.27
23	8.242	4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	7.69
24	8.877	2(3H)-Furanone, dihydro-4-hydroxy-	2.61
25	9.017	3-Pyridinol, 6-methyl-	0.43
26	9.239	4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	0.51
27	9.489	5-(Hydroxymethyl)dihydro-2(3H)-furanone	4.57

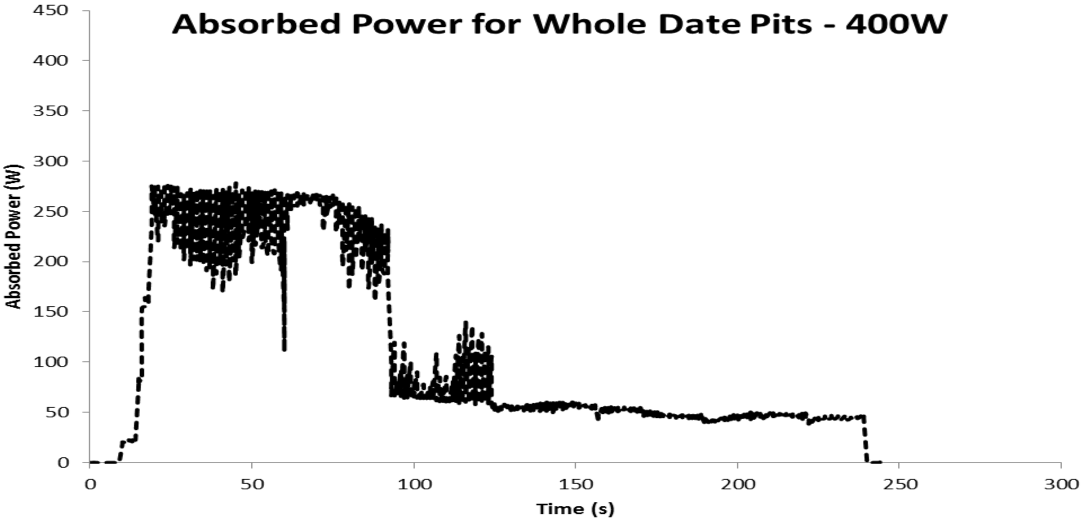
28	9.641	Catechol	8.35
29	10.043	Coumaran	0.44
30	10.416	5-Hydroxymethylfurfural	5.49
31	11.698	Resorcinol	0.45
32	11.844	Dianhydromannitol	0.36
33	12.561	l-Gala-l-ido-octose	0.18
34	13.426	Syringol	0.77
35	16.385	Melezitose	0.39
36	17.579	d-Mannose	0.46
37	18.64	Dodecanoic acid	0.25
38	26.305	Tetradecanoic acid	0.37
39	26.439	Dodecanoic acid, 3-hydroxy-	0.16
40	26.987	n-Hexadecanoic acid	0.22

C. Raw Data Charts of Dry Microwave Pyrolysis








Absorbed Power for Whole Date Pits - 400W
Absorbed Power (W)
Time (s)
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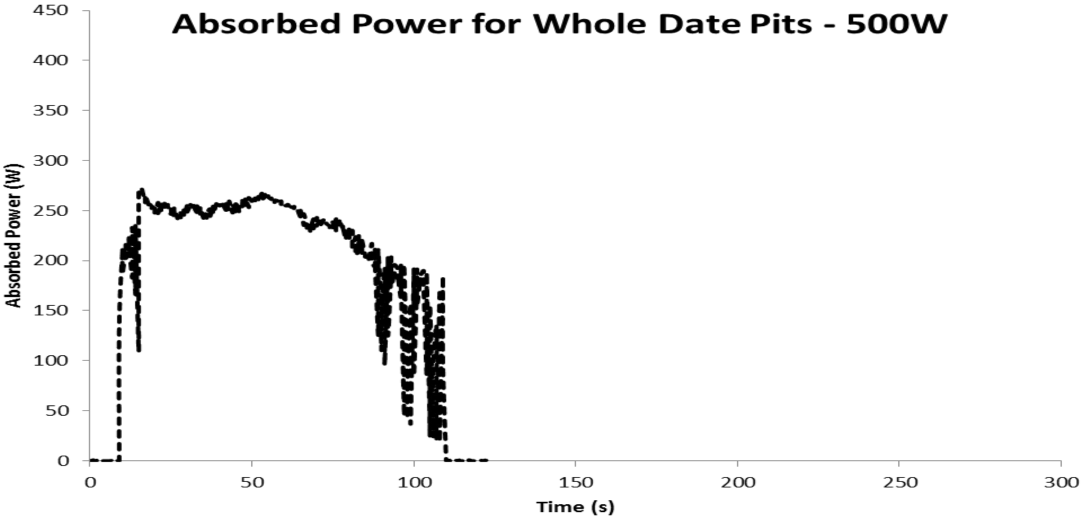
50
100
150
200
250
300
350
400
450
0
50
100
150
200
250
300


Absorbed Power for Whole Date Pits - 500W
Absorbed Power (W)
Time (s)
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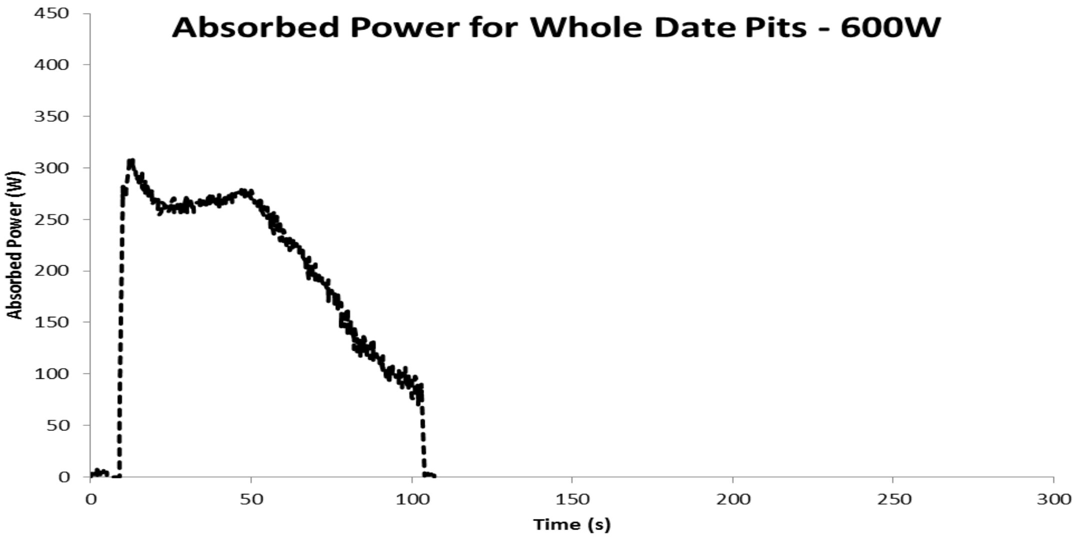
100
150
200
250
300
350
400
450
0
50
100
150
200
250
300


Absorbed Power for Whole Date Pits - 600W
Absorbed Power (W)
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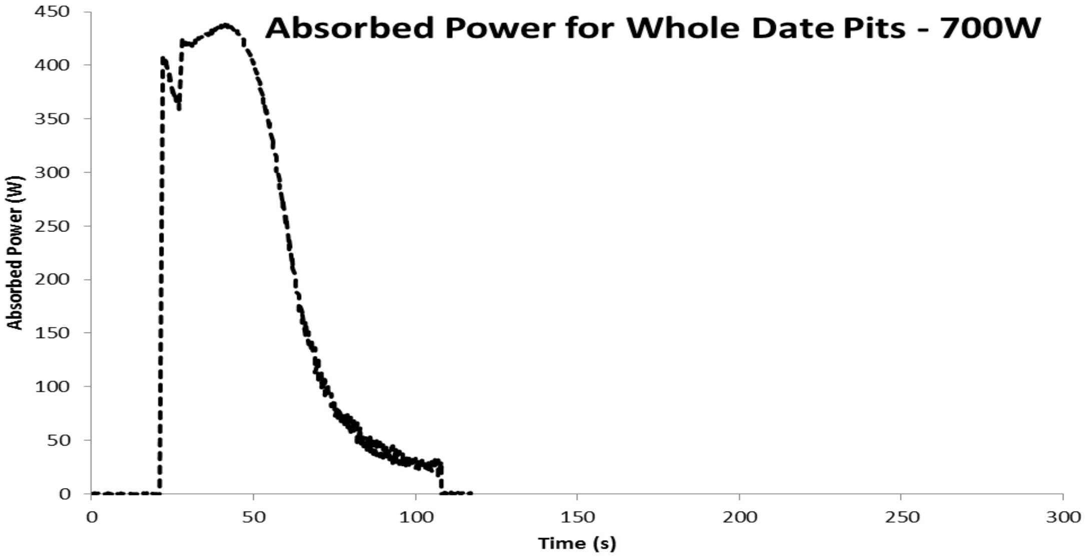
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Time (s)


Absorbed Power for Whole Date Pits - 700W
Absorbed Power (W)
450
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Time (s)