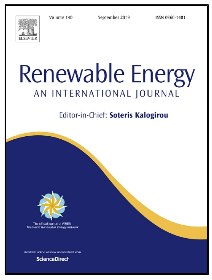
Accepted Manuscript



Fast pyrolysis of date palm (*Phoenix dactylifera*) waste in a bubbling fluidized bed reactor

Yassir Makkawi, Yehya El Sayed, Mubarak Salih, Paul Nancarrow, Scott Banks, Tony Bridgwater

PII: S0960-1481(19)30687-1

DOI: 10.1016/j.renene.2019.05.028

Reference: RENE 11620

To appear in: *Renewable Energy*

Received Date: 11 October 2018

Accepted Date: 07 May 2019

Please cite this article as: Yassir Makkawi, Yehya El Sayed, Mubarak Salih, Paul Nancarrow, Scott Banks, Tony Bridgwater, Fast pyrolysis of date palm (*Phoenix dactylifera*) waste in a bubbling fluidized bed reactor, *Renewable Energy* (2019), doi: 10.1016/j.renene.2019.05.028

Fast pyrolysis of date palm (*Phoenix dactylifera*) waste in a bubbling fluidized bed reactor

Yassir Makkawi [a,*], Yehya El Sayed [b], Mubarak Salih [a], Paul Nancarrow [a], Scott Banks [c], Tony Bridgwater [c]

[a] Chemical Engineering Department, College of Engineering, American University of Sharjah, P.O. Box 26666, Sharjah, United Arab Emirates (UAE).
[b] Department of Biology, Chemistry and Environmental Science, College of Arts and Sciences, American University of Sharjah, P.O. Box 26666, Sharjah, United Arab Emirates (UAE).
[c] European Bioenergy Research Institute (EBRI), Aston University, Birmingham, B4 7ET, United Kingdom (UK)

Abstract

This study presents the first experimental investigation of date palm (*Phoenix dactylifera*) waste fast pyrolysis in a bubbling fluidized bed reactor. The physiochemical characteristics of the feedstock (from cultivars grown in the Emirate of Sharjah in the UAE), including three anatomical parts of the plant, namely, leaves, leaf stems and empty fruit bunches, have been first analyzed and compared to other popular type of biomass. These components have been subjected to fast pyrolysis and mass balances have been derived. The fast pyrolysis products (bio-oil, and non-condensable gas) have been analyzed in terms of their chemical composition, thermogravimetric profiles, and energy content. The overall product distribution in mass percentage at the pyrolysis temperature of 525 ºC was found to be 38.8% bio-oil (including 10.4% reaction water), 37.2% biochar and 24.0% non-condensable gas. The overall energy conversion efficiency (ratio of energy content in the product to that in the feedstock) was found to be 87.0%, thus indicative of the good potential of converting the date palm waste to energy while eliminating the negative environmental impact and cost associated with waste disposal.

Keywords: fast pyrolysis, renewable energy, date palm waste, biomass, fluidized bed reactor, biofuels.

* Corresponding author: Tel.: +97165152167; fax: +97165152979. E-mail address: ymakkawi@aus.edu (Yassir T. Makkawi).

1. Introduction

Palm trees are usually grown in dry, tropical and sub-tropical regions. The fruit produced by the palm trees are called dates, which are consumed as fruits and have been used in the food processing industry to prepare a wide range of products such as date cookies, syrup and paste [1, 2]. According to recent reports, there are more 100−120 million date palm trees worldwide, with the Middle East and North Africa (MENA) countries estimated to have more than 70−90% of the share [1, 3]. Historically, the date palm tree and its fruit have been grown and cultivated as a crop in the MENA region for hundreds of years. In addition to providing fruit rich in nutrients, the various parts of the tree have been used in the past for building boats, shelter and shades for human as well as producing some commodities such as food trays, rope, fish traps, brushes and furniture. Nowadays, such use is no longer practiced, and therefore, the huge amounts of waste produced annually during the harvesting period are not utilized. Most of the waste is either turned into compost, burned in boilers to generate steam [4] or sent to landfill. Clearly, the last two options are not environmentally friendly due to the associated emissions of greenhouse gases.

Several studies have looked at the alternatives to deal with the date palm waste. This includes using the palm tree components as precursors for the development of activated adsorbents as carbon or as a feedstock for biofuel and biochar. The produced material by the first method showed no unique structural features compared to the available commercial adsorbents [6, 7]. Since palm tree waste is known to be composed of hemicellulose, lignin, and cellulose, it should represent a good precursor for biofuel production [8, 9]. In the past few years, there has been growing interest in the waste-to-energy generation, especially through thermochemical conversion. Fast pyrolysis is one of the thermochemical conversion processes that allows the conversion of solid biomass into fuel in an oxygen-limited environment]. The process is conventionally carried out at temperatures higher than 500 °C to produce pyrolysis gas and vapors, and solid biochar. Upon rapid cooling and condensation, the former can be converted into liquid bio-oil and a permanent gas, which can be used for energy generation [10], while the biochar can be used as a soil amendment [11−13].

The variation of the fast pyrolysis operating conditions has also been widely reported to influence the distribution of the final products (biochar, bio-oil and permanent gas). For instance, pyrolysis at temperatures higher than 700 °C and a residence time in the range of 1−2 s favors the formation of a fuel gas (a process commonly referred to as pyrolytic gasification), while a lower temperature of typically around 500 °C and a shorter hot vapor residence time favours the formation of bio-oil. At a much longer residence time and a lower temperature, the process predominately produces biochar (carbonization) through slow pyrolysis [14]. Besides the effect of temperature and residence time, the quality and quantity of the pyrolysis products are dictated by the source and quality of the feedstock [15]. Therefore, in pyrolysis of date palm waste, the products may significantly vary depending on the ecological region in which the tree constituents are cultivated [16]. Of particular impact is the effect of ash in the biomass which catalytically cracks organic vapors to water and CO_2 thus reducing liquid yield and quality.

During recent decades, there have been numerous studies concerning the pyrolysis of different biomass feedstocks for various applications (e,g. Heidari et al. [17], Mesa-Perez et al. [18], Fernandes et al. [19], Abu Baker and Titiloye [20], Madhu et al. [21], Açikalin et al. [22], and Choudhury et al. [23]); however, only a few examined the potential of date palm waste and its characteristics relevant to the fast pyrolysis process. Table 1 summarizes the most recent studies related to the pyrolysis and characterization of date palm tree waste. The date palm tree is quite different to the oil palm tree, which is widely reported in the literature for vegetable oil production and chemicals. To the best of the authors' knowledge, so far, there is not a single study on fast pyrolysis of date palm in bubbling fluidized bed reactors. This type of reactor is widely used at industrial scale due to its high processing capacity and enhanced mixing. There are also conflicting reports on the chemical and physical characteristics of date palm waste and its potentials for energy production through thermochemical conversion. For example, Babiker et al. [24] found significant differences in the thermal decomposition behaviour of six different types of date palm seeds from four different regions (Tunisia, Algeria, Saudi Arabia and Iran). Nasser [25] reported that the chemical constituents of the midribs (lower part of the stem) from date palm cultivates grown in Saudi Arabia are similar to other lignocellulose material, but with lower density, higher ash contents and higher extractives level. While the latter is desirable as it increases the feedstock heating value, the high ash and low density both negatively impact the fuel value index (FVI) (see the above comment about ash); hence, limiting the potentials of the palm tree midribs as a feedstock for energy generation. On the other hand, Sait et al. [26] studied three parts of the date palm tree, namely the leaves, seed and leaves stem. They described the first two as potentially more suitable for fast pyrolysis and combustion compared to the leaves stem, which was found to have lower calorific values and volatile content. El May et al. [27] used thermogravimetric analysis (TGA) to derive the thermochemical conversion kinetics of date palm leaves and rachis (middle part of the stem) and to assess their suitability for the production of biofuel and activated carbons. The overall thermal decomposition profile and content of the volatiles in both parts of the plant were comparable to many woody biomasses. Most recently, Bensidhom et al. [28] reported one of the very few studies on thermal conversion of date palm waste in a fixed bed pyrolysis reactor. The study investigated the pyrolysis (at 500 ºC) of various date palm wastes from cultivates grown in Tunisia. The results showed that the chemical constituents of leaves, empty fruit bunches and rachis are similar, except in ash content, which was found to be considerably higher in the leaves; around twice the quantity found in the other parts of the plant waste. In comparing the overall pyrolysis yield of bio-oil, biochar and permanent gas, the later was found to be high in the case of leaves, at the expense of lowering the quantity of bio-oil. The bio-oil yield from the other parts of the plant was very similar, which suggest a possible correlation between the chemical constituents of the feedstock and the quality and distribution of the products. The permanent gas was also described to be of good fuel properties due to the existence of high fractions of carbon monoxide and methane.

This study presents comprehensive experimental work on the characterization and fast pyrolysis of a date palm tree waste. Three different anatomical parts of the date palm tree, namely, leaves, empty fruit bunches, and leaf stems, were first analyzed for their physio-chemical characteristics using various advanced analytical techniques. The feedstock was then fast pyrolyzed in a bubbling fluidized bed reactor at 525 ºC. Finally, the study concludes with a section discussing the quality of the product bio-oil and non-condensable gas. Most of the analysis was carried out in comparison to other biomass and their pyrolysis products.

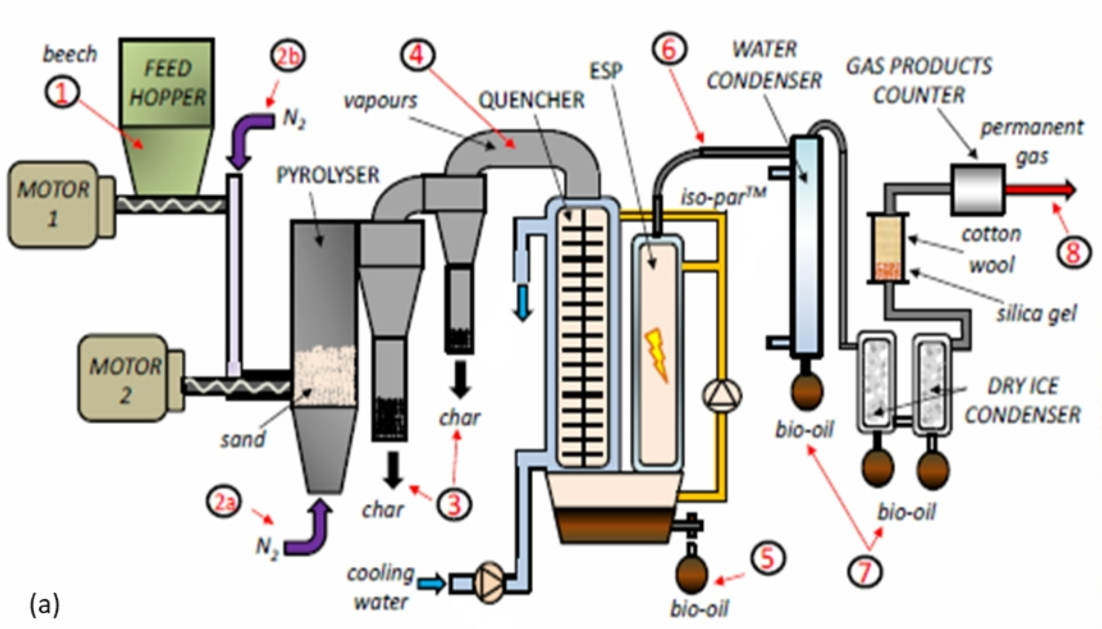
2. Experimental

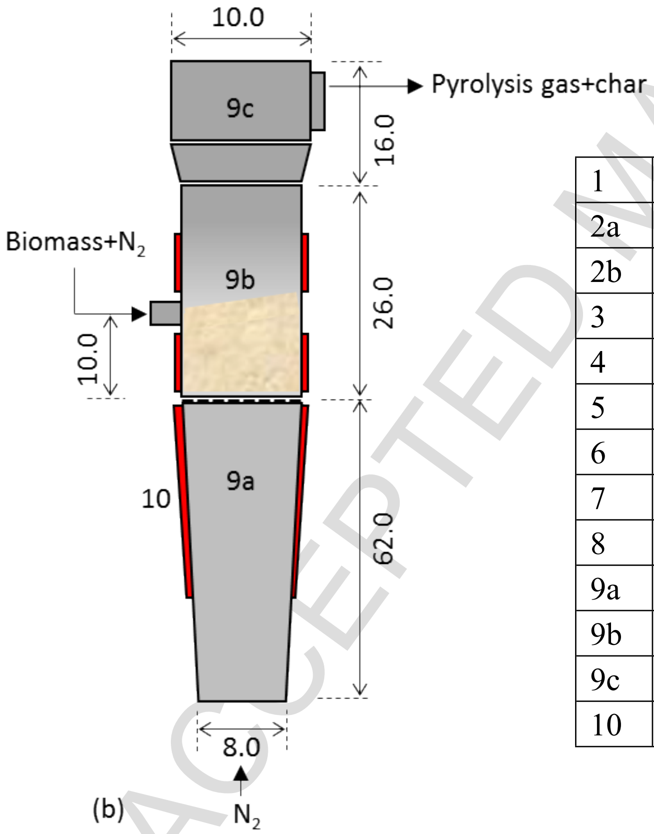
2.1. Fluidized bed reactor

The fast pyrolysis experiment was carried out at the European Bioenergy Research Institute (EBRI) in Aston University, Birmingham, UK. Fig. 1 shows the details of the bubbling fluidized bed reactor used (maximum throughput of 1 kg/h) and the overall arrangement of the set-up including the downstream gas cleaning and cooling/condensation system.

Table 1. Summary of studies on date palm tree waste characteristics and pyrolysis.

Main subject of the study	Analysis type/approach	Main findings	Authors
Pyrolysis of date palm waste	- Fixed bed reactor - Pyrolysis product characteristics	- Bio-oil could be used as fuel after upgrading - Good combustion properties of the permanent gas	Bensidhom et al. [28]
Characterization of different parts of date palm	- Proximate analysis - Thermogravimetric analysis	- Highest extractives in leaflets, followed by date stone. - Ash ranged from 1.4%–15.2% (date stone - leaves) - Thermal decomposition completed below 500 °C, with the exception of leaves, which had highest extractives.	Nasser et al. [9]
Characterization of palm midribs	- Physical/Chemical properties - Statistical analysis	- High levels of extractive - High ash content - Not attractive for energy production	Nasser [25]
Pyrolysis characteristics of six different date palm seeds (DPSs)	- Thermogravimetric analysis - Physical/Chemical properties - Heating value	- A wide range of differences in physiochemical properties. - High volatile compounds and energy densities.	Babiker et al. [24]
Pyrolysis and combustion kinetics of various parts of date palm tree	- Thermogravimetric analysis - Proximate/ultimate analysis - FT-IR analysis of chemical functional groups.	- Date seeds and leaf can potential suitable for biofuel and biochar production. - Stem has low combustion and pyrolysis characteristics due to high moisture content	Sait et al. [26]
Characterization, kinetics and thermal properties of date palm leaflets and rachis.	- Thermogravimetric analysis - Elemental compositions - Kinetic parameters	- Characteristics of leaflets and rachis decomposition - Rate law of decomposition under inert and atmospheric conditions.	El May et al. [27]





1	Biomass hopper
2a	Fluidizing nitrogen
2b	Nitrogen for biomass conveying
3	Cyclones and char pots
4	Pyrolysis gas line
5	Bio-oil collection
6	Non-condensable gas line
7	Condensed light hydrocarbons
8	Permanent pyrolysis gas
9a	Nitrogen preheating section
9b	Fluidized bed reactor
9c	Disengagement section
10	Heating elements

Fig. 1. Biomass pyrolysis system (maximum throughput of 1 kg/h) (a) Overall arrangement of the biomass feeding, pyrolysis reactor and downstream processing (with permission from Atsonios et al. [29]) (b) fluidized bed reactor (all dimensions are in centimeters).

The fluidized bed reactor, which is made of stainless steel 316, consisted of quartz sand as the bed material. Nitrogen gas was used as the fluidizing medium, which was preheated by passing it through a baffled electrically-heated chamber (section 9a in Fig. 1b). Two additional electric heaters, each producing controllable heat input up to 1000 W, were placed externally to the fluidized bed section to maintain the reactor at the required pyrolysis temperature. The heaters were insulated by BCTEX fleece material. The biomass feeding system consisted of two screw feeders and a dropping tube; the first metering screw conveys the biomass from the hopper to the dropping tube and the second faster screw conveys the biomass into the reactor (Section 9b in Fig. 1b) at around 10 cm above the gas distributor. A transparent window placed in the biomass dropping tube allowed monitoring of solid flow rates and ensuring continuous feeding of the biomass. The top of the reactor (Section 9c in Fig. 1) was designed with a slightly larger diameter to allow for disengagement of the sand from the gas.

The downstream gas treatment system consists of two externally heated cyclones with char pots; the first cyclone captures the coarse char while the second one eliminates the remaining finer char particles. This is followed by a quench, electrostatic precipitator (EPS), a water-cooled condenser, 2 dry ice/acetone condensers, packed bed silica gel absorbent, a cotton wool filter to ensure maximum removal of aerosols and a gas meter for recording of the non-condensable gas flow rate. The quench was cooled externally by circulating water and internally by direct contact of the pyrolysis gas with recycled ISOPAR (an inert and immiscible hydrocarbon fluid). To allow for online gas analysis, the final gas exit pipe was equipped with sampling point connected to a gas chromatograph (GC) (Type: Varian CP 4900 Micro–GC) with a thermal conductivity detector (TCD) and two columns (Varian CP–5A molsieve and CP–PortaPLOT).

2.2. Preparation of date palm waste

The date palm tree waste used in this work was collected from various trees grown at the American University of Sharjah campus (Sharjah, UAE) during the peak of palm cultivation and trimming season (July–August). The collected waste consisted of leaves, leaves stems and empty fruit bunches, as shown in Fig. 2a. On average, each palm tree produces 6–10 empty fruit bunches and 12–15 stems, with each stem having around 120–240 leaves [8, 9]. Collectively, these represent around 15–35 kg annual waste per tree.

The waste samples were first dried for a couple of days in an open-air atmosphere and under direct sunlight with a peak temperature around 45 °C, during the daytime. The dried material was then chopped into small pieces before being reduced to particles using a cutting mill (Type: Retsch - SM 200), then sieved to particle size in the range of 0.5–1.0 mm (equivalent diameter) using a vibrating shaker. In terms of grinding power, the leaves were found to consume less energy due to its soft nature, while the stem, which is typically hard wood when dried, required longer processing time and higher grinding power to achieve the same particle size. The physical appearance and properties of the final ground biomass mixture consisting of the three parts of the waste is shown in Fig. 2b.

2.3. Fast pyrolysis procedure and reactor operating conditions

Prior to the experiment, the reactor was filled with quartz sand of the size range 0.60 – 0.71 mm. The packed static bed height was 9.3 cm above the gas distributor. The fluidizing nitrogen gas was preheated to 600 °C to raise the reactor bed to the desired temperature. The main fluidizing nitrogen flow rate was 50.0 L min^{-1}. Additional nitrogen, at the rate of 17.0 L min^{-1} was introduced at the biomass feeding point to create an inert environment and positive pressure. The total nitrogen flow allowed the reactor to be fluidized at 0.485 m s^{-1} velcoity (~ 1.6 time the minimum fluidization velocity); this gives a gas residence time of ~1 s, which is within the range recommended for fast pyrolysis [14]. The quartz sand bed was fluidized with the hot nitrogen for around 1 h to achieve a bed temperature of 525 °C. The fast pyrolysis was commenced by feeding the biomass to the reactor at the rate of 0.3 kg h^{-1}. This rate was found to be suitable to ensure continuous feeding of the highly fibrous biomass particles. During the experiment, the temperature and pressure readings at the various positions within the reactor and downstream were monitored and logged for further analysis (see Fig. 3a). The products leaving the reactor passed through the two cyclones with char pots attached at the bottom to collect the entrained particles (biochar). Both of the cyclones and char pots were externally heated to keep the temperature above 350 ºC. The fast pyrolysis gas then passed through an ISOPAR quench column followed by a wet-walled electrostatic precipitator (ESP) where aerosols, entrained by the fast pyrolysis gas, are coalesced and removed by the ISOPAR circulating between the quench and ESP). The condensed bio-oil was continually collected in the closed container at the bottom of the cooling system. The permanent gas then passes through a water-cooled condenser at 15 ºC, two dry ice-acetone condensers at -70 ºC and finally through the silica gel and cotton wool filters at ambient conditions. The composition of the non-condensable gas was determined online at 150 s intervals using a micro GC before being finally sent to a flare system (see Fig. 3b). Table 2 summarizes the reactor operating conditions.

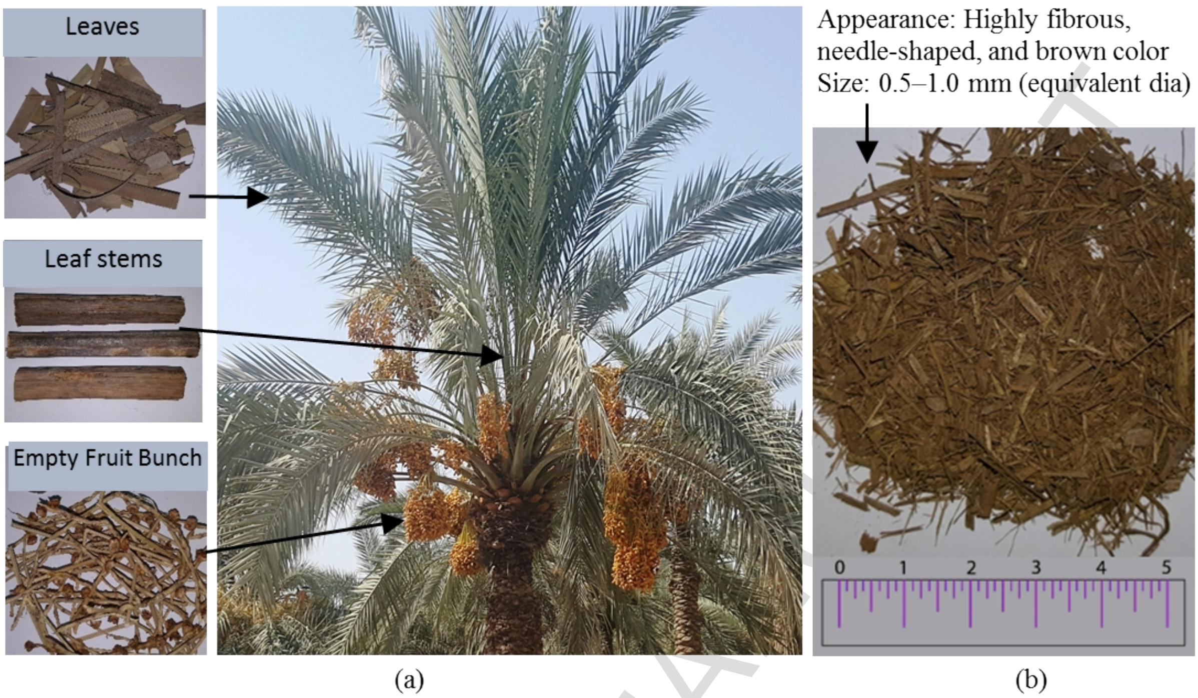


Fig. 2. (a) Date palm tree and samples of the three parts of the wastes used in this study. (b) Ground biomass mixture of the date palm waste consisting of equal fractions of the leaves, leaf stems and empty fruit bunches.

Table 2. Summary of the reactor operating conditions.

Parameter	Operating condition
Biomass particle diameter (mm)	0.60-0.71
Biomass feed temperature (°C)	27
Nitrogen temperature at inlet to preheater (°C)	25
Nitrogen temperature at inlet to the reactor (°C)	600
Average reactor temperature (°C)	525
Cyclones and char pots temperatures (°C)	350
Biomass feed rate (kg h^{-1})	0.30
Total nitrogen feed rate (L min^{-1})	67
Total external reactor heating power (W)	2000

3. Instruments and analysis methods

3.1. Proximate analysis

The proximate analysis of the biomass was carried out to determine the mass of moisture (M), volatiles (V), fixed carbon (FC) and ash in the biomass. The moisture and volatile mass contents were determined by measuring the weight loss using a thermal analyzer (TGA 4000 Instrument, Perkin Elmer, USA). Following ASTM D7582 standard procedure, around 10–20 mg of biomass was placed in a crucible inside the thermal analyzer furnace and subjected to programmed heating at the rate of 10 °C min-1 up to a maximum temperature of 900 °C. The obtained thermogravimetric (TG) curves represent the percentage weight loss caused by desorption of moisture, release of volatiles and decomposition of surface functional groups during progressive heating. The differential thermogravimetric (DTG) curves were obtained from the TG data. The estimated biomass moisture content was also confirmed by oven drying in air at 105 °C according to ASTM D 3173 standard procedure [30]. All of the proximate analysis data were determined from triplicate measurements and expressed in mass percentage. The TG analysis was also applied to the produced bio-oil to gain an insight into the thermal decomposition behavior of the product.

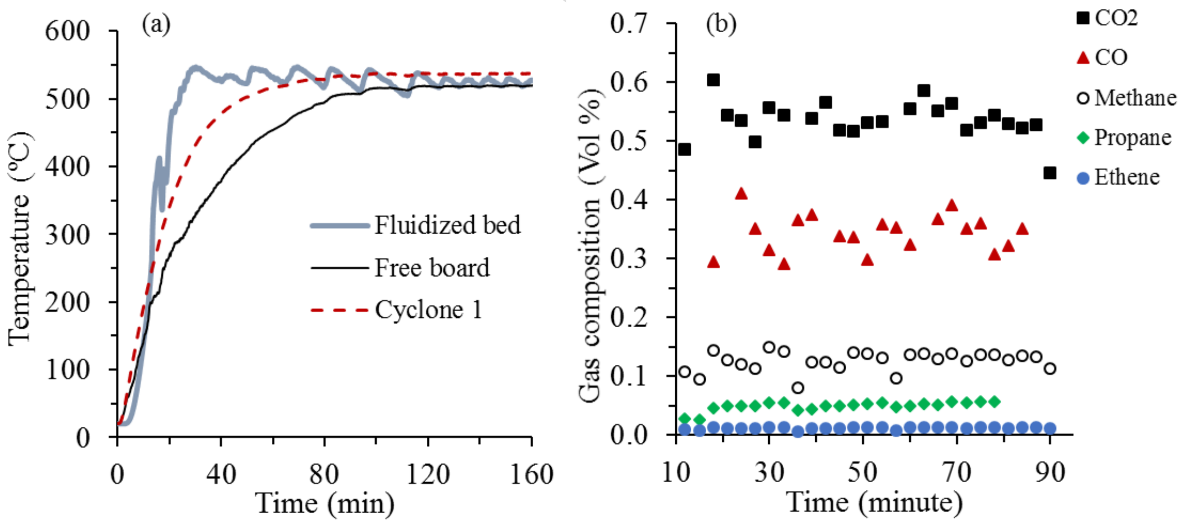


Fig. 3. Examples of recorded data during the pyrolysis experiment (a) Temperature profiles recorded at the reactor, freeboard and first cyclone including the first 40 minutes (heating time) prior to feeding the biomass (b) Composition of the non-condensable gas (main compounds) based on the overall gas including the fluidizing nitrogen.

The ash content of the feedstock was determined by combusting 1.5 g of biomass according to ASTM D 3174-12 standard procedure [31]. The sample was placed in a porcelain crucible and combusted in a muffle furnace (Type: Vecstar furnace– model PF1) at a temperature of 550 ±10 °C. Finally, once the mass percentage of moisture, volatiles and ash was determined, the percentage of fixed carbon was estimated by difference as follows:

$$FC\% = 100 - (M\% + V\% + Ash\%). \tag{1}$$

3.2. Ultimate analysis

The ultimate analysis was carried out to determine the mass of carbon, hydrogen, nitrogen, sulphur and oxygen (C, H, N, S and O) in the biomass and the product bio-oil. The samples were analysed by an external company (MEDAC, UK) using a Carlo-Erba EA1108 CHNS–O analyser employing complete oxidation followed by separation and quantification using chromatographic column and thermal conductivity detector (TCD) flushed by Helium gas. The oxygen was determined by difference.

3.3. Determination of the heating values

The higher heating value (HHV) of the biomass and the fast pyrolysis products (bio-oil and biochar) were determined using a IKA–C1 static jacket oxygen bomb calorimeter. The standard HHV of the permanent fast pyrolysis gas was calculated using the molar concentration of the combustible components in the gas as follows [32]:

$$HHV\ (MJ/m^3) = 12.76\ H_2\ mol\% + 12.63\ CO\ mol\% + 39.76\ CH_4\ mol\%. \tag{2}$$

3.4. Analysis of the permanent gas and bio-oil composition

An on-line Varian CP 4900 Micro–GC micro–gas chromatograph with TCD and two columns (Varian CP–5A molsieve and CP–Porta PLOT) was used to determine the composition of the non-condensable gas. The data was recorded online at an interval of 150 s during the fast pyrolysis process.

The chemical composition of the bio-oil was characterized using gas chromatography/mass spectrometry (GC/MS) system (QP2010 Ultra Thermal Desorption–Gas Chromatography–Mass Spectrometry). Approximately, 20 mg of bio-oil was dissolved in 15 mL ethanol. High purity tridecane (>99 % purity and density of 0.756 g/cm^3) was used as an internal standard. The solutions were centrifuged at 2500 rpm and then loaded to the auto sampler where 1 μL is injected into the column. The inlet temperature of the GC was fixed at 280 ºC. Initially, the column temperature was maintained at 60 ºC for 2 minutes and then ramped at a rate of 5 ºC min^{-1} to 300 ºC, which was held constant for 40 minutes. The column used for analysis was a Rtx-1 from Restek (30 m in length, 0.25 µm in thickness, and 0.25 mm in diameter). Helium was used as the carrier gas with a flow rate of 1.24 mL min^{-1}.

The bio-oil water content was determined by Volumetric Karl Fischer (KF) titration. A Mettler Toledo V20 KF titrator with Hydranal (R) K as a working medium and Hydranal (R) Composite 5K as a titrant. All analyses were performed in triplicate.

3.5. Analysis of the yield and conversion efficiency

The percentage mass yield of each of the fast pyrolysis product components (bio-oil, biochar and permanent gas) was calculated based on the mass ratio of the product to the feed biomass (dry basis) as follows:

$$\text{yield}\ (\%) = \frac{\text{mass of product (bio} - \text{oil, biochar or permanent gas)}}{\text{mass of biomass fed}} \times 100. \quad (3)$$

The biomass energy conversion efficiency was calculated based on the ratio of the energy content in the product to that in the feedstock. This was obtained by using the higher heating values (HHV) and the mass of each component (m) as follows:

$$\eta_{eff}\ (\%) = \frac{(\text{m HHV})_{\text{biochar}} + (\text{m HHV})_{\text{bio}-\text{oil}} + (\text{m HHV})_{\text{permanent gas}}}{(\text{m HHV})_{\text{biomass}}} \times 100. \quad (4)$$

4. Results and discussion

4.1. Feedstock characteristics

This section presents the proximate and ultimate analysis in addition to the characterization of the chemical constituents of the various parts of the date palm waste considered in this study. The analysis is presented in comparison with other types of biomass commonly used in pyrolysis for the wider benefit.

4.1.1. Ultimate analysis of the feedstock

Fig. 4 shows the ultimate analysis of the date palm waste, giving the measured elemental mass fractions of carbon, hydrogen, nitrogen and oxygen. Clearly, there are no significant differences between the leaves, leaf stem and fruit bunches in terms of the carbon, hydrogen and oxygen content. The variations in sulphur and nitrogen is relatively high but these elements exist in small quantities. The samples were found to contain 40−45% carbon, 5−6% hydrogen, 0.5−1.5% nitrogen, 0.15−0.25% sulphur and 49−53% oxygen. This is reasonably within the range of the reported literature for date palm, as shown in Table 3. There are very few studies reporting the sulphur content in date palm waste. The ones included in Table 3 suggest that the sulphur content is highest in the leaves. High sulphur carries the risk of increasing corrosion and undesirable gas emissions when utilized in large-scale production. Nevertheless, this range remains comparable to some energy crops, such as miscanthus, which has a sulphur content of 0.28 [33].

Fig. 5 shows a comparison of the ultimate analysis of the date palm waste mixture (consisting of equal fractions of leaves, leaves stem and empty fruit bunches) with various types of waste biomass and energy crops. With the exception of rapeseed and linseed, all of the materials considered appear to have comparable carbon, hydrogen and nitrogen. Again, compared to wider biomass, the palm tree waste mixture is shown to have high sulphur, however, less than that in banana leaves. The oxygen content is also high; close to that reported in cotton shell, rice husk, and to some extent, banana leaves. In biomass fast pyrolysis, high oxygen content in the feedstock promotes the formation of oxygenated compound in the bio-oil, hence may have a negative impact on the bio-oil stability and limit its application as a transportation fuel.

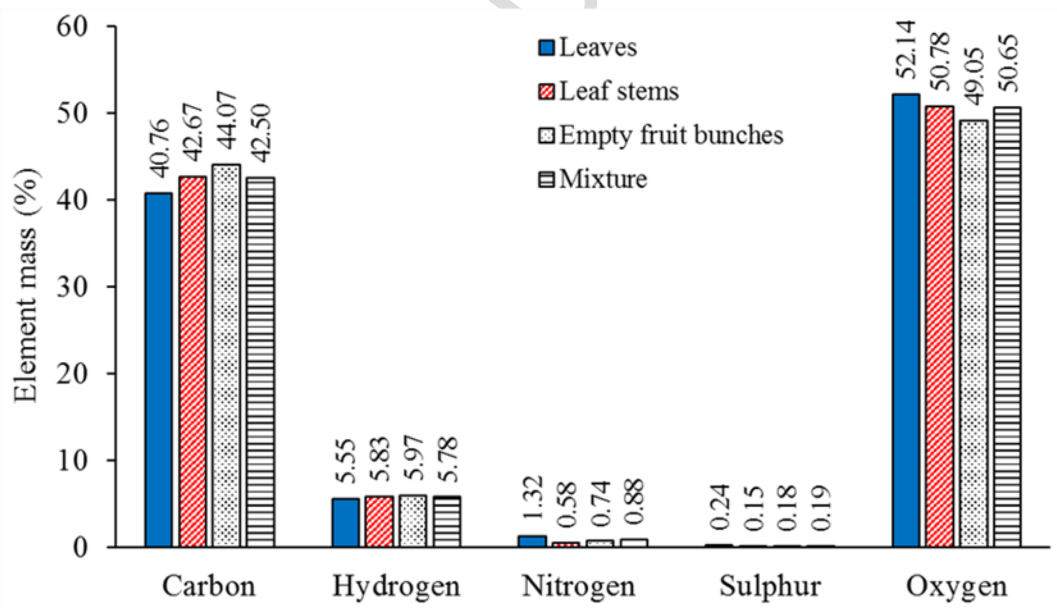


Fig. 4. Ultimate analysis of date palm waste used in this study.

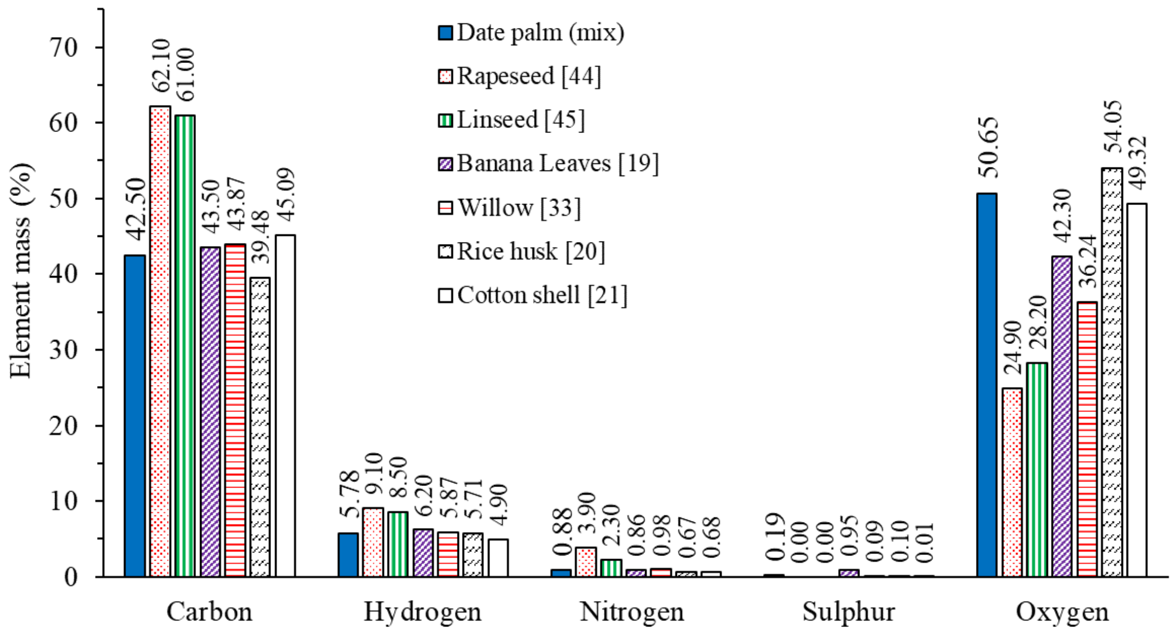


Fig. 5. Comparison of ultimate analysis of the date palm waste (mixture) with various waste biomass and energy crops.

Table 3. Ultimate analysis (mass %) of date palm waste in comparison to reported literature.

Reference	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
	Empty fruit bunches				
Nasser et al. [9][a]	45.58	6.03	0.26	-	48.13
Bensidhom et al. [28][a]	43.49	7.51	0.188	-	52.73
This study	44.07	5.97	0.74	0.18	49.05
	Leaves				
Nasser et al. [9][a]	46.50	5.69	0.66	-	47.15
Bensidhom et al. [28][a]	43.14	7.49	0.19	-	52.71
Sait et al. [26]	49.40	5.80	1.20	1.30	42.30
Hussain et al. [16]	50.40	6.30	1.10	0.40	41.80
This study	40.76	5.55	1.32	0.24	52.14
	Leaf stems				
Nasser et al. [9][a,b]	43.07	5.79	0.28	-	50.87
Sait et al. [28]	36.10	5.20	0.70	0.70	57.20
Hussain et al. [16]	38.10	5.20	0.80	0.30	55.60
This study	42.67	5.83	0.58	0.15	50.78

[a] No data for sulphur
[b] Data average of midrib (leaves stem) base, middle and top

4.1.2. Proximate and Thermogravimetric analysis of the feedstock

Fig. 6 shows the thermogravimetric (TG) data of the percentage mass loss during heating and the corresponding derivative of the mass loss for the three types of date palm waste individually and the mixture. The curves can be interpreted as indicative of the stages of degradation of the main organic compounds in the biomass (hemicellulose, cellulose and lignin) [34]. Clearly, the curves are quite similar in terms of overall trend and there are no significant differences in the transition temperature between the identified stages. Here, it is believed that the first stage up to the temperature of ~110 °C is associated with the release of moisture and therefore can be classified as drying. This is followed by a second stage characterised by a relatively thermally-stable stage with a limited mass loss up to ~200 °C. The major mass loss, which is associated with the devolatilization and decomposition of the chemical constituents of the biomass (cellulose, hemicellulose, and lignin) [34], occurs in stage 3. This appears to commence at around ~200 °C and considerably slows down and tails out beyond ~525 °C, The total percentage mass loss in stage 3 is around 65% and is widely believed as a result of hemicellulose and cellulose degradation [28, 35]. In a Thermogravimetric analysis of date palm waste by Nasser et al. [9], the maximum mass loss was reported to take place within the temperature range of 228−512 °C, which is close to the range found in this study. The data reported by Bensidhom et al. [28] suggested a narrower range for major devolatilization within 220–400 °C. In woody biomass, the hemicellulose is reported to exhibit lower molecular weights, therefore decomposes first within the temperature range of 200–260 °C, then followed by cellulose decomposing within the range of 240–350 °C, and finally lignin decomposing within a wider range of 280–500 °C [35]. In this study, and according to the position of the peaks in the DTG curves shown in Fig. 6b, it is suggested that the degradation of hemicellulose peaks at ~285 °C while the cellulose degradation peaks at ~340 °C. In stage 4, the mass loss beyond ~525 °C and up to 900 °C is the slowest and is believed to be mainly associated with lignin degradation as it is the hardest to thermally degrade compared to the hemicellulose and cellulose [35].

Fig. 7 shows the proximate analysis, giving the moisture, ash, volatiles and fixed carbon contents of the date palm waste. Unlike the ultimate analysis; here the differences between the various parts of the waste (leaves, stem and fruit bunches) is high, particularly, in terms of ash and fixed carbon contents. The leaves have the highest ash (14.4 mass%) and moisture (12.03 mass%) and lowest volatiles (58.17 mass%). This is not surprising since, in almost all plants, the leaves always contain the highest ash, almost double that in the other anatomical parts of the plant [36].

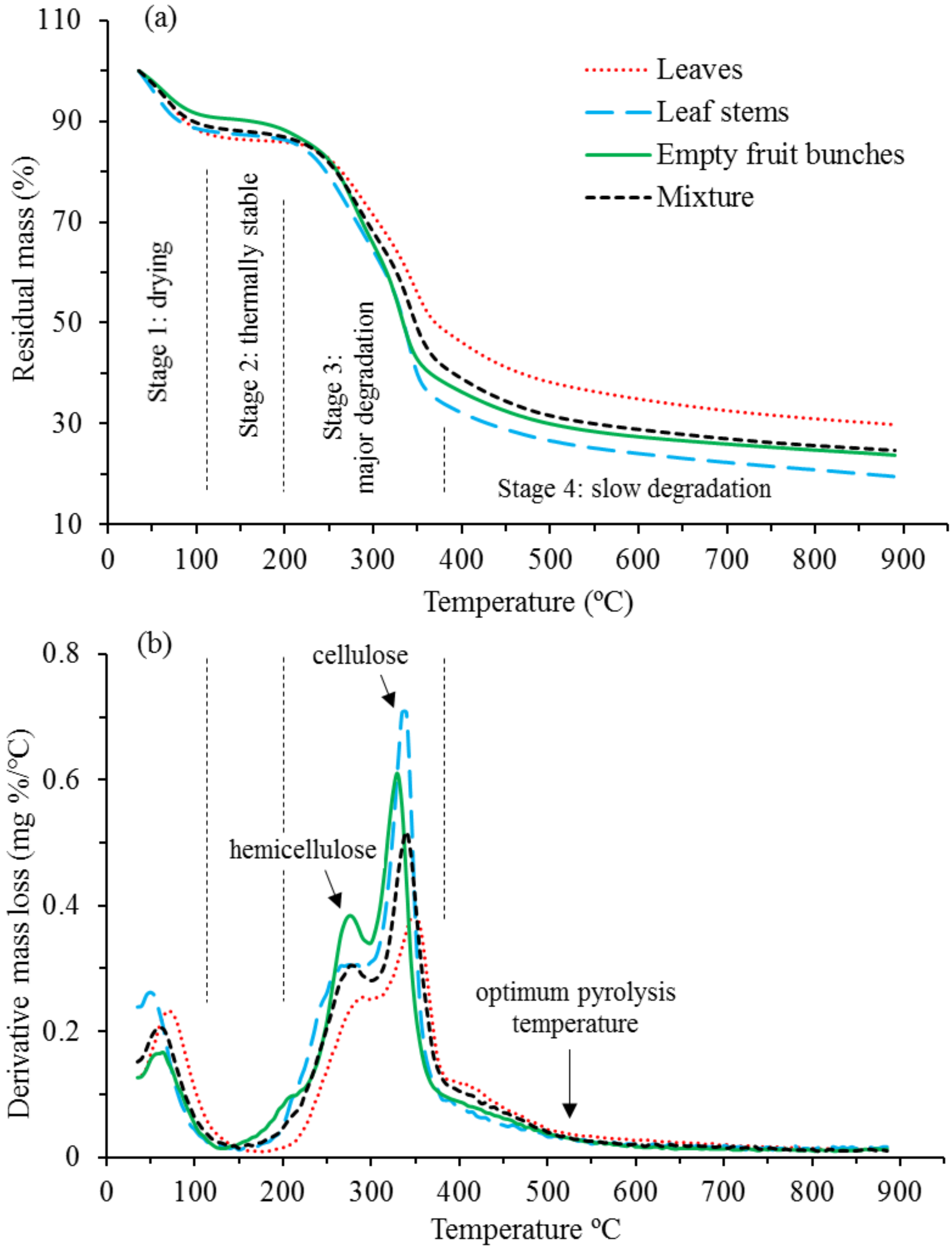


Fig. 6. Thermogravimetric analysis of the date palm waste (a) percentage mass loss (b) derivative mass loss.

Table 4 shows the proximate analysis in comparison with the available literature data on date palm waste. Here, there is sufficient agreement to confirm that the ash content is highest in the leaves and lowest in the empty fruit bunches. However, it is also clear that the data is generally quite scattered, especially with respect to the volatiles content, which is shown to be varying within a wide range of 52.0−88.0 mass%. This can be attributed to the differences in plantation environment and cultivations methods. Therefore, more studies are required to confirm the chemical compositions of the various parts of the plant and perhaps conduct comprehensive studies specifically focused on the classification of the plant potentials for thermochemical conversion according to regions and plantation environment.

In comparison with wider types of biomass, Fig. 8 confirms that date palm waste mixture can be classified as having relatively high ash and low volatile contents. The high ash is mainly due to the presence of leaves, and, to some extent, the leaf stems, in the mixture. It is possible that the lack of rainfall and high evaporation rate in the desert climate of UAE may have contributed to high concentration of minerals in the soil ending up in the leaves and leaf stems, which otherwise, could have been reduced by leaching. Ideally, in fast pyrolysis, it is desirable to have the ash ending up in the biochar to avoid contamination of the product fuel. However, if such biochar ends up in a landfill or is used for soil amendment then such a practice, in the long run, carries the risk of an excessive increase in the soil alkalinity and water contamination by increasing the level of mineral concentrations [37]. On the other hand, if the char or ash is entrained by the pyrolysis gas, then it must be quickly separated to avoid catalytic cracking of the fast pyrolysis gas, which in turn, significantly affects the product distribution by reducing the bio-oil yield [38]. Therefore, the use of the date palm leaves individually as the main feedstock is not highly recommended. Having said that, recent work by the authors on the pyrolysis of empty fruit bunches only (not included here), which is significantly low in ash, have shown negligible differences compared to the products and yield from the pyrolysis of the mixture considered here. Therefore, from a practical point of view, there are no strong justifications to treat each waste stream separately. Furthermore, if the process is to be developed to industrial scale, then segregation or exclusion of the leaves from the mixture will entail extra cost, and most importantly, significantly reduce the available amount of feedstock. Similar view has also been reported by Hussain et al. [16] when discussing the commercial potentials of date palm waste in pyrolysis and combustion applications.

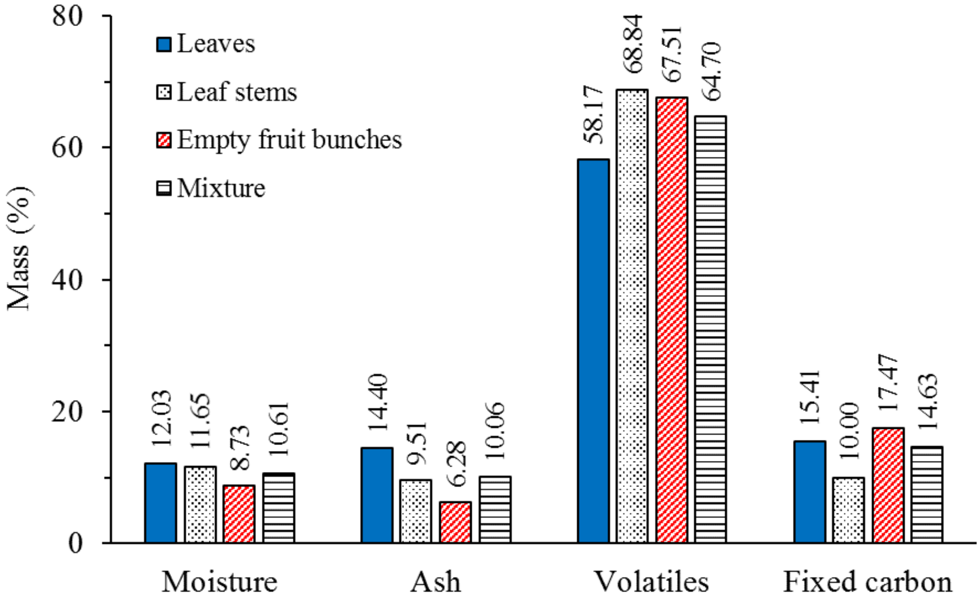


Fig. 7. Proximate analysis of the date palm waste.

Table 4. Comparison of the proximate analysis of this study with the literature data.

Reference	Moisture	Ash	Volatiles	Fixed carbon
	Empty fruit bunches			
Nasser et al. [9][a]	-	1.78	87.48	10.78
Bensidhom et al. [28]	7.68	4.20	81.20	6.92
This study	8.73	6.28	67.51	17.47
	leaves			
Nasser et al. [9][a]	-	15.20	74.29	10.51
Bensidhom et al. [28]	8.50	11.58	72.28	7.64
Sait et al. [26]	17.70	19.20	55.30	7.80
Hussain et al. [16]	5.30	12.10	77.50	6.10
This study	12.03	14.40	58.17	15.41
	Leaf stems			
Nasser et al. [9][a,b]	-	6.69	79.42	13.89
Sait et al. [26]	17.70	19.20	55.30	7.80
Hussain et al. [16]	18.10	20.20	52.10	8.10
El May et al. [27]	12.10	6.00	73.60	8.30
This study	11.65	9.51	68.84	10.00

a Moisture-free basis
b Averaged from frond midrib and frond base

4.1.3. High Heating Value (HHV) of the feedstock

Fig. 9 shows the HHV of date palm waste in comparison with other biomass materials. The various parts of the waste (stem, leaves stem and empty fruit bunches) are clearly very similar in terms of energy content. The leaves are slightly higher in HHV than the stem and empty fruit bunches. In comparison to other biomass, the date palm HHV is clearly lower than the rapeseed and linseed and close to that of the energy crop willow and the vegetable waste banana leaves. This analysis confirms that the date palm has sufficient convertible energy.

4.2. Bio-oil characteristics

This section is focused on assessing the bio-oil in terms of (i) chemical composition; determined by using by GC-MS analysis (ii) thermal decomposition profile and volatilization characteristics; determined by thermogravimetric analysis, and (iii) ultimate analysis, high heating value and water content; determined by CHNS analyser, bomb calorimeter and titration, respectively.

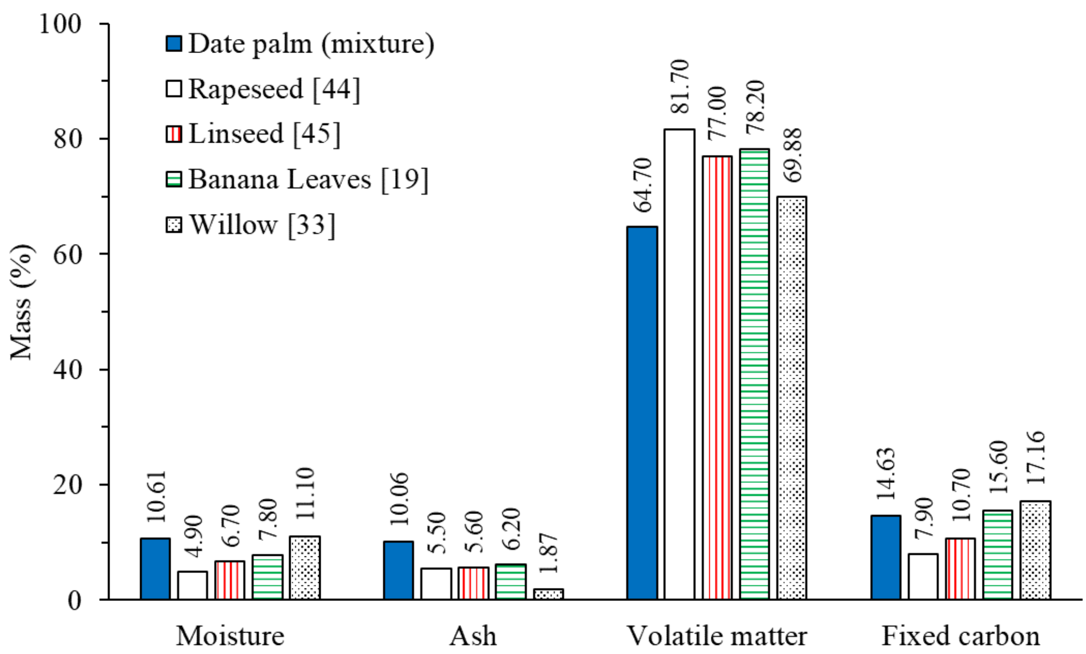


Fig. 8. Proximate analysis of the date palm waste mixture in comparison with other waste biomass and energy crop.

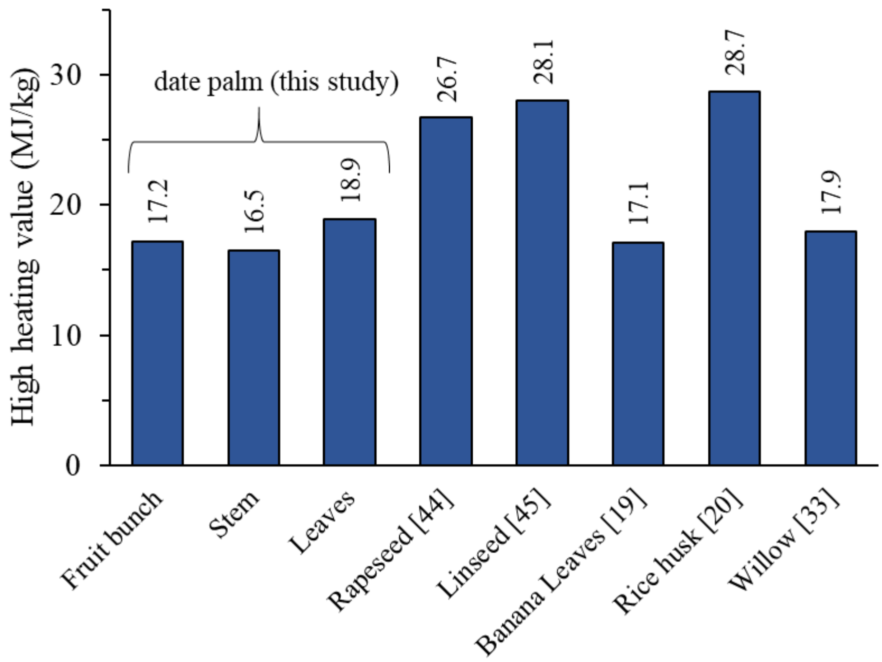


Fig. 9. High heating value of the date palm waste in comparison to other waste biomass and energy crop.

4.2.1 Chemical composition

Unlike the conventional crude oil derived from fossil fuels (such as petroleum and coal oil), the chemical composition of bio-oil from fast pyrolysis of biomass is highly complex and contains a vast array of chemical compounds and a water fraction. Bio-oil is generally known to be thermally instable and has high tendency to polymerize when exposed to air [35,39]. In this study, the GC-MS analysis of the product bio-oil revealed the existence of more than 140 different compounds with clear detectable peaks. Table 5 shows only the main 30 compounds (representing around 75% of the oil) arranged based on their percent by mass. This was calculated using the internal standard and percent normalization parameters. Undecane was used as an internal standard at an amount that provided the peak area relative to those obtained for the compounds in the bio-oil sample. The calculated mass percent is assumed to be indicative of the mass fraction, hence this is a semi-quantitative evaluation. It should also be noted that this is the first published data on the chemical composition of fast pyrolysis bio-oil produced from date palm tree waste.

Overall, the most abundant compounds identified in the bio-oil can be classified into monosaccharides, hydrocarbons, phenols, alcohols and ketones, which are commonly reported as natural extract from plant sources. For example, D-Allose is a monosaccharide that is reported as one of the compounds detected in oil obtained from pyrolysis of palm shell [40]. Apocynin is known to be natural inhibitor of the production of superoxide (O_2^-) in biological systems. It is a methoxy-substituted compound of Catechol, which is also identified in the bio-oil sample. The presence of oxygenated compounds is prevalent and this is generally known to negatively affect the bio-oil stability and energy content besides increasing its corrosivity [14]. On the other hand, the identified compounds with the highest abundance in the bio-oil have the ability to reduce reactive oxygen, and hence may play a role as an antioxidant in the bio-oil or mixed with biodiesel to improve stability. Furthermore, such compounds can be extracted and used as commercial antioxidants in various types of bio-lubricants.

4.2.2. Thermo-gravimetric (TG) analysis of the bio-oil

Fig. 10 shows the thermogravimetric (TG) profile of the bio-oil. The mass and derivative mass loss curves clearly support the GC-MS analysis where most of the compounds seem to vaporize at temperatures below 280 °C, which is the injector temperature. The profiles indicate that the bio-oil thermally decomposes following two stages. Stage 1, in which the major and rapid mass loss takes place below ~200 °C (~60% loss), is characterised by three distinct peaks in the derivative curve at 80 °C, 125 °C and 190 °C. These peaks are most likely due to the volatilization of major components that are of low boiling point. It is interesting that similar peaks within the same temperature range have been reported by Lu et al. [41] when analysing bio-oil produced from rice husk. In stage 2, the remaining weight loss (~20%) is gradual and relatively much slower, taking place beyond the temperature of ~300 °C. This is believed to be a result of thermal cracking of the heavy compounds in the bio-oil mixture.

Table 5. Main chemical compounds found in date palm bio-oil.

Peak#	Name	%
1	D-Allose	11.09
2	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	10.78
3	Apocynin	9.76
4	Catechol	4.19
5	Cyclopropane, 1-methyl-1-(2-methylpropyl)-2-nonyl-	3.68
6	Pentadecane, 2,6,10,14-tetramethyl-	3.34
7	1,2,4-Trimethoxybenzene	3.15
8	Hexadecane, 1-chloro-	3.11
9	1,2-Cyclopentanedione, 3-methyl-	3.06
10	.alpha.-D-Glucopyranose, 4-O-.beta.-D-galactopyranosyl-	2.80
11	1-Tetradecene	2.33
12	Benzene, 1,2,3-trimethoxy-5-methyl-	2.30
13	1,2-Benzenediol, 4-methyl-	2.01
14	Heptadecane, 2,6,10,15-tetramethyl-	2.00
15	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.93
16	Desaspidinol	1.85
17	Sulfurous acid, 2-ethylhexyl tetradecyl ester	1.75
18	2(5H)-Furanone	1.67
19	Phenol, 2-methoxy-	1.60
20	2-Methoxy-5-methylphenol	1.51
21	Decane, 3,8-dimethyl-	1.35
22	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.30
23	1,3-Benzenediol, 2-methyl-	1.23
24	Nonadecane, 9-methyl-	1.17
25	Heneicosane	1.16
26	Hexane, 1-(hexyloxy)-3-methyl-	1.10
27	1-Nonadecene	1.08
28	1-Tridecene	1.07
29	3,5-Dimethoxyacetophenone	1.06
30	Hexadecane, 2,6,10,14-tetramethyl-	1.04
31	Others	14.52

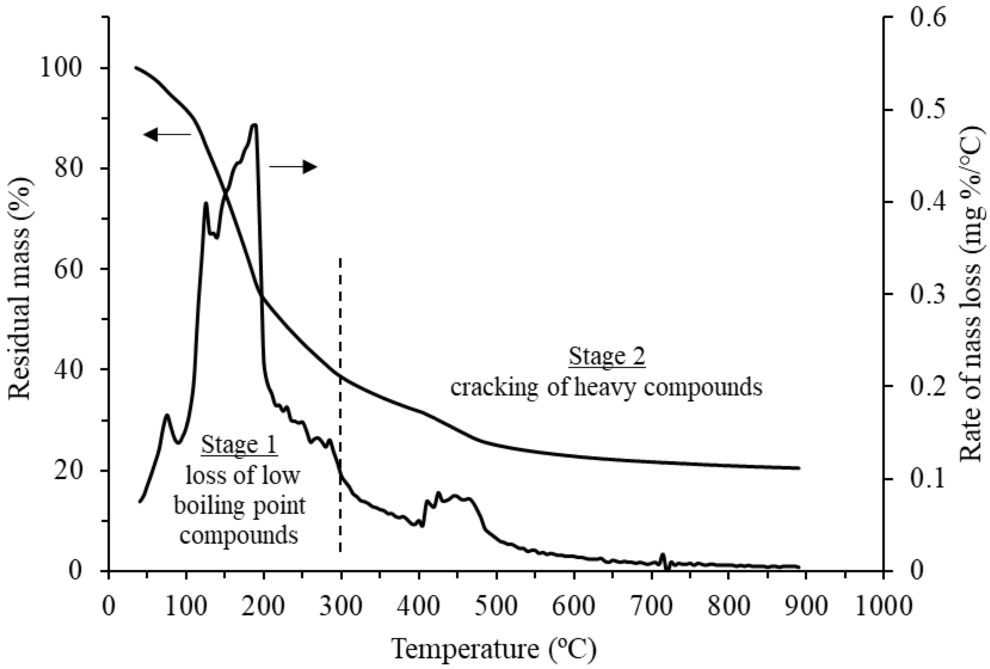


Fig. 10. Thermogravimetric analysis of mass and derivative mass loss of date palm bio-oil.

4.2.3. High Heating Value (HHV) of the bio-oil

The high heating value (HHV) of the product bio-oil and the date palm waste mixture feed is shown in Fig. 11 in comparison with reported literature for other biomass. The HHV of the date palm waste bio-oil was found to be 20.88 MJ/kg. This falls within the low-intermediate range of HHV compared to bio-oil from other waste biomass and energy crop. Interestingly, the data confirm a strong correlation between the HHV of the feedstock and the product bio-oil. A similar correlation between the feedstock and the quality of the pyrolysis oil has been recently revealed in details by Li et al. [42] in a comprehensive study covering a wide range of biomass material.

4.2.4. Ultimate analysis and water content

The ultimate analysis (elemental composition) and the water content of the date palm waste bio-oil in comparison with literature data are given in Table 6. The date palm waste bio-oil is clearly high in oxygen content and contains a relatively low water fraction. This is also the reason behind the existence of many oxygenated compounds that are of low boiling point, as noted earlier. Most interesting, there seems to be a strong evidence of a relation (correlation) between the bio-oil characteristics and the elemental composition that dictates the quality of the bio-oil. This is despite the difference in the pyrolysis conditions (i.e. temperature, reactor type, heating rate, etc.). Such a correlation has also been observed by Di Blasi et al. [43] and Bensidhom et al. [28]. It is also interesting to note the great similarity between the elemental composition of the bio-oil produced from the date palm waste and the banana leaves. Both materials appear to produce highly oxygenated bio-oil with relatively low calorific value and carbon content. On the other hand, the rapeseed and linseed feedstock, which also agree on their elemental composition, have been found to produce closely matched bio-oil; high in carbon content and heating value and low in oxygen content. This confirms that the biomass type and its characteristics play the major role in defining the quality of the pyrolysis bio-oil.

4.3. Product yield and conversion efficiency

Fig. 12a shows the distribution (mass %) of the overall fast pyrolysis product. The overall mass balance closure was 86.6%. This is satisfactory compared to the reported literature for similar size pyrolysis reactors. For example, Atsonios et al [29], reported a mass balance closure of 93.3%, for fast pyrolysis of beech wood in the same reactor used in this study. Yang et al. [46] produced a mass balance of around 90% in an auger reactor, while Prymak [47] reported low values between 60-85% in a fluidized bed reactor. In general, mass balance loss in most pyrolysis reactors is difficult to avoid due to unrecoverable condensed liquid and solid in the pyrolysis system connecting pipes and fittings.

The overall product consisted of 37.2% char, 38.8% bio-oil and 24.0% non-condensable gas (all on dry and ash free basis). Note that the bio-oil includes 10.4% reaction water. A typical range of bio-oil yield from fast pyrolysis of biomass is reported to fall within 60−75 mass% [48], and this is usually form low ash biomass. Therefore the bio-oil yield achieved here can be classified as low. Recently, Bensidhom et al. [28] reported lower bio-oil yield in the range of 17.0–25.9 mass% when pyrolysing various Tunisian date palm waste in a fixed bed reactor at the temperature range of 500–700 °C. This low bio-oil yield in the specific case could be a result of the nature of the reactor and operating conditions used, i.e. fixed bed with long gas residence time. However, the low bio-oil yield from date palm waste, in general, could be attributed to the negative impact of the high ash and fixed carbon contents in the feedstock, which come at the expense of volatile content. It is worth noting that other types of biomass materials of high ash and fixed carbon, such as rice husk [49] and oil palm leaves [50], have also been reported to produce low bio-oil yield. Other reasons could be related to the biomass particle size used in this experiment since some studies have shown a consistent increase in the bio-oil yield as the particle size decreases, which in turn, enhance the heating and devolatilization rates. The mass fraction of the non-condensable gas (24.0%) is slightly towards the high range compared to wider reported data for fast pyrolysis (10-20%).

Fig. 12b shows the detailed composition of the non-condensable gas. The gas consist mainly of carbon dioxide (54.55%) and low concentration of combustible gases (27.40% carbon monoxide, 5.39% methane, 5.68% propane and lower fractions of other gases). The calculated high heating value (HHV) of the gas is 8.89 MJ/kg, which is less than half of the heating value of the bio-oil and the feed biomass mixture (20.88 MJ/kg and 17.52 MJ/kg, respectively). The high fraction of carbon dioxide in the gas is mainly due to the high oxygen content in the feedstock, and possibly, the cracking of organics by the ash. It is most likely that this could be reduced by operating at a higher temperature since high pyrolysis temperature favors the formation of carbon monoxide [51], but at the same time this may come at the expense of reducing the bio-oil yield by thermal cracking of heavy hydrocarbons in the pyrolysis gas [14].

Finally, in order to access the overall energy efficiency of the process, the pyrolysis conversion efficiency was calculated using the energy content in the products and the feedstock, as defined earlier in Eq.4. The total amount of the processed date palm waste was 257.8 g (dry basis) and the total recovered products was as follows: 86.5 g bio-oil, 83.1 g char and 53.6 g non-condensable gas, all on dry and ash free basis, giving a mass balance closure of 86.6%, as noted above. The measure HHV of the bio-oil and char was 20.88 MJ/kg and 19.76 MJ/kg, respectively. The HHV of the non-condensable gas, calculated by Eq. 2, was found to be 8.9 MJ/kg. Accordingly, the calculated overall conversion efficiency was 87.0%. Such a high conversion efficiency makes the date palm waste and the proposed pyrolysis process economically attractive for large scale processing.

5. Conclusion

In this study, fast pyrolysis of date palm (Phoenix dactylifera) waste have been carried out in a reactor operating at an average reactor temperature of 525 °C. This is the first comprehensive study on the pyrolysis of this feedstock in a fluidized bed reactor. The waste biomass was collected from date palm trees grown in the United Arab Emirates, one of the major producing countries of date palm fruit worldwide. The study first looked at the detailed physical and chemical characteristics of the waste, which consisted of three different anatomical parts of the plant. Comparison of the proximate and ultimate analysis of the three parts of the plant have shown great similarity but with the leaves relatively consisting of much higher ash. In comparison to other types of biomass and energy crops, the date palm waste mixture can be classified as of high ash, high oxygen, low volatiles and average heating value. The fast pyrolysis product, in mass fractions, was found to consist of 38.75% bio-oil (including 10.39%

reaction water), 37.23% biochar and 24.02% non-condensable gas. The GC-MS analysis revealed for the first time the detailed composition of the date palm pyrolysis oil, which consisted of at least 140 detectable compounds, with the major ones being D-Allose (monosaccharide), phenols, catechol and apocynin. The latter two compounds are of particular interest due to their antioxidation characteristics. The bio-oil heating value was 20.88 MJ/kg, which falls within the low-intermediate range for most fast pyrolysis bio-oils; however, the oxygen content was high, and this may have a negative impact on the oil stability and corrosivity. Our on-going research is now focused on parametric analysis to assess the effect of reaction temperature on the pyrolysis products quality and distribution. Future work will also look into the application side of the pyrolysis products, such as the potential use of the bio-oil as a blend with biodiesel for combustion engines, the long-term aging and stability of the oil and the potential use of the biochar for soil amendment, especially in desert climate.

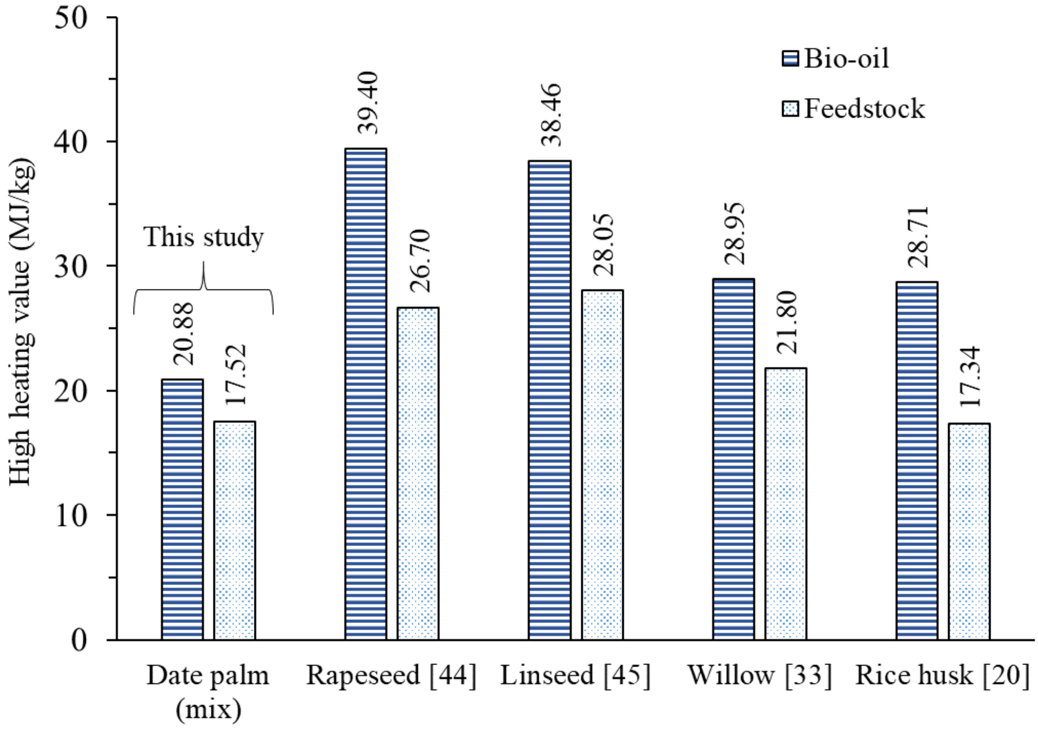


Fig. 11. High heating value of the bio-oil from the date palm mixture in comparison with an energy crop and other waste biomass materials.

Table 6. Ultimate analysis (moisture free) and water content of the date palm waste bio-oil in comparison to bio-oil from other biomass materials.

	This study	Rapeseed[44,a]	Linseed[45,b]	Rice husk[20,c]

Elemental analysis				
C	49.63	73.10	75.42	23.38
H	7.35	11.50	10.26	10.39
N	1.09	4.70	1.50	0.51
S	0.10	0	0	<0.10
O	41.84	10.70	13.80	65.63
Water content	10.40	-	-	52.60

[a] Reactor: well-swept fixed bed tubular reactor; temperature: 550 °C; Heating rate 30 °C min^{-1}; biomass: rapeseed; biomass size: 0.425-0.85 mm; carrier gas flow rate of 100 cm^3 min^{-1}.
[b] Reactor: well-swept resistively heated fixed bed reactor; temperature 550 °C; Heating rate 300 °C min^{-1}; biomass: linseed; biomass size: 0.6-1.8 mm; carrier gas flow rate of 100 cm^3 min^{-1}
[c] Reactor: fixed bed reactor; Temperature 450 °C; heating rate 25 °C min^{-1}; Biomass: rice husk; Biomass size: 355-849 mm; carrier gas flow rate of 50 cm^3 min^{-1}.

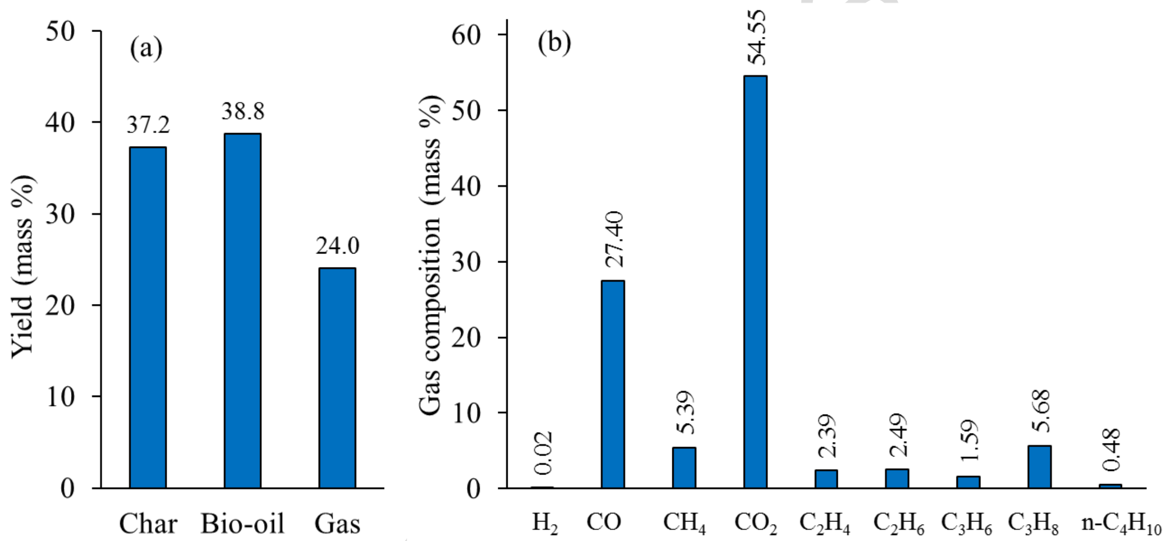


Fig. 12. (a) Overall product yield and (b) composition of the non-condensable gas from the fast pyrolysis of date palm waste.

Acknowledgments

The authors would like to thank the American University of Sharjah (AUS) for funding the project under Grant FRG 16-R-27.

References

[1] Ghnimi, S.; Umer, S.; Karimb, A.; Kamal-Eldina, A. Date fruit (Phoenix dactylifera L.): An underutilized food seeking industrial valorization. NFS Journal 2017, 6, 1–10

[2] Kamal-Eldin, A.; Hashim, I. B.; Mohamed, I. O. Processing and utilization of palm date fruits for edible applications, Recent Pat. Food Nutr. Agric. 2012, 4, 78–86.

[3] El-Juhany, L. I. Degradation of date palm trees and date production in Arab countries: causes and potential rehabilitation. Aust. J. Basic Appl. Sci. 2010, 4, 3998–4010.

[4] Galiwango, E.; Al-Marzouqi, A. H.; Abu-Omar, M. M.; Khaleel, A. A.; Abdel Rahman, N. S. Estimating Combustion Kinetics of UAE Date Palm tree Biomass using Thermogravimetric Analysis, Journal of Natural Sciences Research 2017, 7, 106–120.

[5] Khalifa, N.; Yousef, L. F. A short report on changes of quality indicators for a sandy textured soil after treatment with biochar produced from fronds of date palm. Energy Procedia. 2015, 74, 960–965.

[6] Shoaib, M.; Al-Swaidan, H. M. Ramp rate influence on synthesis of sliced porous activated carbon from date palm tree by physical activation method. Asian J. Chem. 2014, 26, 5295–5297.

[7] Houache, O.; Al-Maamari, R.; Al-Rashidi, B.; Jibril, B. Study of date palm stem as raw material in preparation of activated carbon. J. Eng. Res. 2008, 6, 47–51.

[8] Barreveld, W. H. Date palm products; FAO Agricultural Services Bulletin book (101); Food and Agricultural Organization: Rome, Italy, 1993.

[9] Nasser, R. A.; Salem, M. Z. M.; Hiziroglu, S.; Al-Mefarrej, H. A.; Mohareb, A. S.; Alam, M.; Aref, I. M. Chemical analysis of different parts of date palm (Phoenix dactylifera L.) using ultimate, proximate and thermogravimetric techniques for energy production. Energies. 2016, 9, 374–388.

[10] Jahirul, M. I.; Rasul, M. G.; Chowdhury, A. A.; Ashwath, N. Biofuels production through biomass pyrolysis – A technological review. Energies. 2012, 5, 4952–5001.

[11] Al-Wabel, M. I.; Usman, A. R. A.; El-Naggar, A. H.; Aly, A. A.; Ibrahim, H. M.; Elmaghraby, S.; Al-Omran, A. Conocarpus biochar as soil amendment for reducing heavy metal availability and uptake by maize plants. Saudi J. Biol. Sci. 2015, 22, 503–511.

[12] Laird, D. A. The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. Agron. J. 2008, 100, 178–181.

[13] Jeffery, S.; Verheijen, F. G. A.; van der Velde, M.; Bastos, A. C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agric. Ecosyst. Environ. 2011, 144, 175–187.

[14] Bridgwater, A. V. Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J. 2003, 91, 87–102.

[15] Kenney, K. L.; Smith, W. A.; Gresham, G. L.; Westover, T. L. Understanding biomass feedstock variability. Biofuels. 2013, 4, 111–127.

[16] Hussain, A.; Farooq, A.; Bassyouni, M. I.; Sait, H. H.; El-Wafa, M. A.; Hasan, S. W.; Ani, F. N. Pyrolysis of Saudi Arabian date palm tree waste: A viable option for converting waste into wealth. Life. Sci. J. 2014, 11, 667–671.

[17] Heidari, A.; Stahl, R.; Younesi, H.; Rashidi, A.; Troeger, N.; Ghoreyshi, A. A. Effect of process conditions on product yield and composition of fast pyrolysis of Eucalyptus grandis in fluidized bed reactor. J. Ind. Eng. Chem. 2014, 20, 2594–2602.

[18] Mesa-Pérez, J. M.; Rocha, J. D.; Barbosa-Cortez, L. A.; Penedo-Medina, M.; Luengo, C. A.; Cascarosa, E. Fast oxidation pyrolysis of sugar cane straw in a fluidized bed reactor. Appl. Therm. Eng. 2013, 56, 167–175.

[19] Fernandes, E. R. K.; Marangoni, C.; Souza, O.; Sellin, N. Thermochemical characterization of banana leaves as a potential energy source. Energy Convers. Manag. 2013, 75, 603–608.

[20] Abu Bakar, M. S.; Titiloye, J. O. Catalytic pyrolysis of rice husk for bio-oil production. J. Anal. Appl Pyrolysis. 2013, 103, 362–368.

[21] Madhu, P.; Kanagasabapathy, H.; Neethi Manickam, I. Cotton shell utilization as a source of biomass energy for bio-oil by flash pyrolysis on electrically heated fluidized bed reactor. J. Mater. Cycles Waste Manag. 2016, 18, 146–155.

[22] Açikalin, K.; Karaca, F.; Bolat, E. Pyrolysis of pistachio shell: effect of pyrolysis conditions and analysis of products. Fuel. 2012, 95, 169–177.

[23] Choudhury, N. D.; Chutia, R. S.; Bhaskar, T.; Kataki, R. Pyrolysis of jute dust: effect of reaction parameters and analysis of products. J. Mater. Cycles Waste Manag. 2014, 16, 449–459.

[24] Babiker, M. E.; Aziz A. R. A.; Heikal, M.; Yusup, S.; Abakar, M. Pyrolysis characteristics of Phoenix dactylifera date palm seeds using thermogravimetric analysis (TGA). Int. J. Environ. Sci. Technol. 2013, 4, 521–524.

[25] Nasser, R. A. An evaluation of the use of midribs from common date palm cultivars grown in Saudi Arabia for energy production. Bioresour. 2014, 9, 4343–4357.

[26] Sait, H. H.; Hussain, A.; Salema, A. A.; Ani, F. N. Pyrolysis and combustion kinetics of date palm biomass using thermogravimetric analysis. Bioresour. Technol. 2012, 118, 382–389.

[27] El May, Y.; Jeguirim, M.; Dorge, S.; Trouve, G.; Said, R. Thermogravimetric analysis and kinetic study on palm of Phoenix dactylifera L. In proceedings of the 7th Mediterranean Combustion Symposium (MCS 7) in Italy, Chia Laguna, Cagliari, Sardinia, Italy, Semptember 11-15, 2011.

[28] Bensidhom, G.; Ben Hassen-Trabelsi, A.; Alper, K.; Sghairoun, M.; Zaafouri, K.; Trabelsi, I. Pyrolysis of date palm waste in a fixed-bed reactor: characterization of pyrolytic products. Bioresour. Technol. 2018, 247, 363–369.

[29] Atsonios, K.; Panopoulos, K. D.; Bridgwater, A. V.; Kakaras, E. Biomass fast pyrolysis energy balance of a 1 Kg/h test rig. Int. J. Thermodyn. 2015, 18, 267–275.

[30] ASTM D 3173/D 3173-17a, Standard test method for moisture in the analysis sample of coal and coke, ASTM International, West Conshohocken, PA, 2017, www.astm.org

[31] ASTM D 3174-12, Standard test method for ash in the analysis sample of coal and coke from coal, ASTM International, West Conshohocken, PA, 2012, www.astm.org

[32] Waldheim, L. Nilsson, T. Heating value of gases from biomass gasification; 2001.

[33] Karampinis, E.; Vamvuka, D.; Sfakiotakis, S.; Grammelis, P.; Itskos, G.; Kakaras, E. Comparative study of combustion on five energy crops and Greek lignite. Energy & Fuels. 2012, 26, 869–878.

[34] Tonbul, Y. J. Pyrolysis of pistachio shell as biomass. Therm. Anal. Calorim. 2008, 91, 641–647.

[35] Mohan, D.; Pittman, C. U.; Steele, P. H. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy & Fuels. 2006, 20, 848–889.

[36] Monti, A.; Di Virgilio, N.; Venturi, G. Mineral composition and ash content of six major energy crops. Biomass and Bioenergy. 2008, 32, 216–223.

[37] Woldetsadik1, D,; Drechsel, P.; Keraita, B..; Marschner, B.; Itanna, F.; Gebrekidan, H. Effects of biochar and alkaline amendments on cadmium immobilization, selected nutrient and cadmium concentrations of lettuce (Lactuca sativa) in two contrasting soils. SpringerPlus. 2016, 5:397

[38] Bridgwater, A. V.; Meier D.; Radlein, D.; An overview of fast pyrolysis of biomass, Organic Geochemistry, 1999, 30, 1479–1493.

[39] Zhang, L.; Liu, R.; Yin, R.; Mei, Y. Upgrading of bio-oil from biomass fast pyrolysis in China: A review. Renew Sust Energ Rev. 2013, 24, 66–72.

[40] Abnisa, F. Study of pyrolysis of oil palm solid wastes and co-pyrolysis of palm shell with plastic and tyre waste, PhD thesis, 2015, University of Malaya, Kuala Lumpur.

[41] Lu, Q.; Yang, X.; Zhu, X. J. Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk. Anal. Appl. Pyrolysis. 2008, 82, 191–198.

[42] Li, J.; Chen, Y.; Yang, H.; Zhu, D.; Chen, X.; Wang, X.; Chen, H. Correlation of feedstock and bio-oil compound distribution. Energy & Fuels. 2017, 31, 7093–7100.

[43] Di Blasi, C.; Branca, C.; Santoro, A.; Gonzalez Hernandez, E. Pyrolytic behaviour and products of some wood varieties. Combust. Flame. 2001, 124, 165–177.

[44] Onay, O.; Kockar, O. M. Slow, fast and flash pyrolysis of rapeseed. Renew. Energy. 2003, 28, 2417–2433.

[45] Acikgoz, C.; Onay, O.; Kockar, O. M. Fast pyrolysis of linseed: product yields and compositions. J. Anal. Appl. Pyrolysis. 2004, 71, 417–429.

[46] Yang, Y.; Heavenb, S.; Venetsaneasb, N.; Banks, C. J.; Bridgwater, A. V. Slow pyrolysis of organic fraction of municipal solid waste (OFMSW): Characterisation of products and screening of the aqueous liquid product for anaerobic digestion, Applied Energy 213 (2018) 158–168

[47] Prymak, E. Energy from Switchgrass: Bio-Mass Conversion Analysis. Swarthmore College. Dept. of Engineering, thesis, 2013.

[48] Mohan, D.; Pittman, C.U.; Steele, P.H. Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy and Fuels, 2006, 20, 848-889.

[49] Tsai, W. T.; Lee, M. K.; Chang, Y. M. Fast pyrolysis of rice husk: product yields and compositions. Bioresour. Technol. 2007, 98, 22–28.

[50] Abnisa, F.; Arami-Niya, A.; Wan Daud, W. M. A.; Sahu, J. N.; Noor, I. M. Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis. Energy Convers. Manag. 2013, 76, 1073–1082.

[51] Fu, P.; Yi, W.; Bai, X.; Li, Z.; Hu, S.; Xiang, J. Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues, Bioresource Technology. 2011, 102, 8211–8219.

Highlights

- This is the first study on fast pyrolysis of date palm (Phoenix dactylifera) waste in a bubbling fluidized bed reactor.
- The bio-oil consisted of high concentration of D-Allose, Phenol, Apocynin and Catechol compounds.
- The overall product yield was 38.8% bio-oil, 37.2% biochar and 24.0% non-condensable gas.
- The biomass has high ash content, which may negatively impact the bio-oil yield.