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ORIGINAL ARTICLE

Comparison of bio-oils derived from crop digestate treated through conventional and microwave pyrolysis as an alternative route for further waste valorization

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Abstract
A total of 120,000 tonnes per year of crop waste from contaminated land has been used as a feedstock for anaerobic digestion (AD). This produces only around 20% of biogas from the total crop and results in a large amount of digestate with heavy metal content. This crop digestate was analyzed across a calendar year to identify the variation in composition, and any potential high-value components that could be targeted for recovery. The chemical characterization revealed that approximately 65% of this residual waste is lignocellulosic material (20% hemicellulose, 24% cellulose, 24% lignin) and about 10% is ash, with no observable difference across the seasons. Three different pyrolysis technologies were studied with the same crop digestate as alternative route to maximize the value of this solid residue by transforming this lignocellulosic material into further bio-based products. Slow pyrolysis at operating temperatures between 355 and 530 °C resulted in bio-oil yields of 35–46% wt, fast pyrolysis at 460–560 °C produced 36–40% wt, and microwave pyrolysis using a power input of 500 and 700 W generated 8–27% wt from the digestate. Chemical compounds found in these bio-oils were categorized into seven chemical groups: acids, aldehydes and ketones, alcohols, furans, sugars, phenolics, and others. This analytical study opens other scenarios to explore the upgrading of these pyrolytic bio-oils for green product generation from the same waste.

Keywords Anaerobic digestion · Decarbonization · Lignocellulose · Circular economy

1 Introduction

Anaerobic digestion (AD) has been promoted as a key processing technology for green energy production with positive impacts in term of reducing the amount that goes to landfill, and also providing a continuous source of primary green energy [1–5]. In AD processes, the main product from the system is biogas, but there is also a significant amount residual solid waste named *digestate*, which has been used mainly as fertilizer due to the nitrogen- and phosphorus-rich material content [6, 7]. This has been considered a net-zero emission system due to reuse of waste: digestate is employed to amend the soil where plants or crops are growing and then these are used for renewable energy generation. Analysis of this cycle has already been carried out because this system also absorbs carbon dioxide as the vegetation growing in this soil is then improved and amended [8, 9]. Since the loop including this waste is closed, it can be considered to have the potential to form the basis of a genuine circular economy. Although this sounds promising, analysis of biobased fertilizers by Kataki et al. [10] mentioned that there are still barriers to implementation of this type of waste due to strict legislation, the lack of incentives for use of this for soil restoration, and inadequate investment in research and design to complete a whole cycle of nutrient recovery. Despite the fact that this activity can have a positive impact on the environment due to soil improvement, some of this waste-based fertilizer needs to be transported which results in an additional cost to that of spreading it on the soil, and sometimes then, the process has no profit for the producers.

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These practices also have a negative impact on the digestate effectiveness. Ammonia can arise from digestate, which could lead to emissions and air quality issues in the area where it is utilized [11]. Although the Department for Business, Energy & Industrial Strategy in the UK considers a positive impact implementing AD for biomethane production and digestate as fertilizer, it is also looking for solutions to tackle ammonia emissions from this agriculture practice to reduce air pollution, which in long-term can cause harm to habitats and ecosystems [12].

Chemical composition of digestate varies across AD systems due to different organic waste used for biogas production. This can be food waste, agricultural residue, manure, municipal solid waste, sewage, or mixtures of diverse sources [13]. The crop waste used in this study was grown on contaminated land and has been used to produce biogas through an AD system. The digestate resulted from this AD has been used as fertilizer, but it is only suitable for use on the same land for further energy crop cultivation due to its heavy metal content.

If this waste can be successfully valorized then this could improve the balance of carbon emissions. There are a number of strategies which might allow for enhancement to treat wastes such as digestate in order to increase its value and use for further processing. Digestate has the potential to be valorized by using it as feedstock for different thermochemical processes, such as pyrolysis, to produce further green bioproducts, and heavy metals present in digestate could be concentrated in the final biochar, and be recovered with further treatment to avoid further environmental contamination [14].

Most of the pyrolysis systems have been studied and employed based on lignocellulose conversion [15–18]. The thermochemical decomposition of each lignocellulosic compound occurs at different temperatures when is subjected to pyrolysis treatments, where also key chemicals are produced. Hemicellulose is decomposed between 200 and 260 °C producing mainly furfural, cellulose is depolymerized in a range of 240–350 °C generating high amount of levoglucosan, and lignin is converted mostly into phenolics in temperatures between 280 and 500 °C [19, 20].

Slow pyrolysis consists of heating the feedstock with a residence time range between 5 and 30 min. Due to the large period during which the biomass is subjected to these high temperatures, more reactions take place where the products formed can be cracked, resulting in enhanced formation of biochar and gas. This type of pyrolysis is employed when the main target is biochar generation, and bio-oil formed from slow pyrolysis is generally considered to be a low-quality product [15, 17, 21]. Fast pyrolysis is employed to produce bio-oil as a main product. It uses a high heating rate and a short processing time, resulting in more condensable product which needs to be recovered to avoid subsequent reactions with the produced biochar. The typical yields of these pyrolysis products (by weight) are 60–75% bio-oil, 15–25% solid biochar, and 10–20% non-condensable gases [15, 17]. One of the main requirements of this thermal process is that the feedstock particle size is reduced to enable sufficient heat transfer to take place within the required low residence time. Larger particle sizes can result in higher production of biochar and water [22, 23]. Microwave pyrolysis is considered an efficient method to process lignocellulosic material to produce a high-quality liquid content, with a high organics content due to a different mechanism of heating. Heat transfer occurs from the center of the biomass due to molecular interaction with an electric field, with products passing through zones of lower temperature that limit the prevalence of secondary reactions [24, 25]. This is different from conventional pyrolysis where heat travels from the surface into the center, and the organic compounds generated are in contact with high temperatures which degrade the bio-oil product [26, 27]. Due to this microwave mechanism, some organics are produced in higher yields when woody biomass is pyrolyzed.

This study evaluates each of the three pyrolysis technologies with digestate, and unlike previous studies uses the same sample of digestate as feedstock and the same analytical techniques to characterize the products. Digestate has a higher ash content than woody biomass (1–3% wt [28, 29]), and the impact of ash is assessed in this work.

2 Materials and methods

2.1 Feedstock

Crop digestate used as feedstock in the three pyrolysis system was collected over a period of 3 to 4 weeks from the Severn Trent Water Anaerobic Digestion facility at Stoke Bardolph, Nottinghamshire, in the United Kingdom. Each collection was characterized individually. Additional crop digestate was sampled during a year for analysis and characterization to detect any variation. The digestate was dried at 105 °C for 24 h, and stored in vacuum-sealed packaging to preserve it and ensure that the material can be stored for several months to be treated in the three pyrolysis technologies implemented in this work. The digestate was prepared according to the available systems for this study and considering the best conditions already implemented in other investigations using lignocellulosic feedstock where equivalent parameters between technologies could maximize the quality of the pyrolytic products from crop digestate.

2.2 *Method for characterization*

A number of methods were implemented to determine different properties of the feedstock employed in the different pyrolysis technologies and the pyrolytic products recovered:

2.2.1 Proximate and ultimate analysis

Proximate composition was performed through thermogravimetric analysis (TGA) using ASTM D7348 [30] employed for loss on ignition (LOI) of solid combustion residues performed by Mayoral et al. [31]. Analysis was carried out in a TGA Q600 with 10–12 mg of sample placed in an alumina crucible. Moisture content was determined by heating the biomass up to 110 °C at 20 °C/min with nitrogen (100 ml/min, 1 bar) holding this temperature for 15 min. Subsequently, at the same heating rate, the temperature was increased to 950 °C and held for 30 min to obtain the volatile matter. After this time the sweep gas was switched to air to calculate fixed carbon and ash content by combusting the remaining material for 15 min. Ultimate analysis was performed using a LECO CHN628 elemental analyzer, which operates by a complete combustion technique with pure oxygen at temperatures up to 1050 °C. This analysis was validated with a certified reference standard BBOT (2,5-di (5-*tert*-butylbenzoxazol-2-yl) thiophene) by LECO with specific composition of carbon (C), nitrogen (N) and hydrogen (H) by processing around 75 mg of this standard in the CHN628. Both analyses were performed in triplicate as a minimum.

2.2.2 Lignocellulosic material

Cellulose and hemicellulose were determined by hydrolysis, extraction, and quantification of the carbohydrates that can be attributed to one particular biopolymer in the source biomass. The remaining material from this extraction was used for lignin determination.

Hydrolysis—carbohydrate extraction Samples were hydrolyzed according to Saeman et al. [32] which comprises two steps. The first was adding a solution of 72% (w/w) H_2SO_4 into the tube with the sample and then incubating at 30 °C for 1 h. The second step consisted of adding water to the sample, after the 1-h incubation, to obtain a 9% (w/w) H_2SO_4 solution which was incubated for 3 h at 100 °C.

A small aliquot of 0.1% (w/v) bromophenol blue in ethanol was added to each sample and the pH was adjusted with barium carbonate until the solution turned a blue color. The solution was filtrated using a 0.45 µm PTFE filter and 2-Deoxy-D-galactose was added as internal standard (IS). Samples were analyzed in duplicate.

Two standard solutions were employed for this analysis with several monosaccharides at concentrations in a range of 0.1 to 0.02 mg/mL for the calibration curves. Standard A consisted of fucose, IS, arabinose, galactose, glucosamine, xylose, N-acetyl-D-galactosamine, and D-galacturonic acid. Standard B comprised IS, rhamnose, galactosamine, glucose, mannose, *N*-acetyl-D-glucosamine, ribose, and D-glucuronic acid.

Carbohydrates were quantified by high performance anion exchange chromatography (HPAEC) using an ICS-5000$^+$ ion chromatography system. The system was equipped with a CarboPac PA1 column (2 × 250 mm) preceded with a CarboPac guard column (2 × 50 mm), and a pulsed electrochemical detector (Dionex, Sunnyvale, USA). The flow rate employed was 0.3 mL/min, and the temperature in the column was 17 °C. The elution in the system was performed next through the following sequence: 0–53 min H_2O, 53–63 min 150 mM NaOH, 63–63.1 min a gradient from 150 to 500 mM NaOH, 63.1–78 min 500 mM NaOH, 78–83 min a gradient from 500 mM NaOH to H_2O, and 83–100 min H_2O. Monosaccharides were detected after the post column addition of 0.5 M NaOH at 0.1 mL/min.

The carbohydrate concentration obtained from this analysis was based on the detection of monosaccharides due to the hydrolysis performed on crop digestate. In order to calculate the concentration on a dry basis of the polysaccharides in the biomass, anhydro correction factors were used: for example 0.88 for C-5 sugars such as xylose and arabinose, and 0.90 for C-6 sugars, such as glucose, galactose, and mannose.

Lignin determination The insoluble lignin (AIL) in the acid hydrolysate was measured by weight as Klason lignin [33] whereas the soluble lignin (ASL) content was determined spectrophotometrically at 205 nm [34]. For calculation of ASL, an extinction coefficient for lignin of 110 L/g.cm at 205 nm was used.

2.2.3 Analysis of pyrolysis products

Bio-oil Bio-oil samples were weighed in a tared 2 mL GC vial. Standards were employed to obtain reliable quantification of the compound in pyrolysis bio-oil, and based on the analytical procedure developed by the National Renewable Energy Laboratory (NREL) [35]. The main standards employed were: furfural (Sigma-Aldrich 185,914), 5-(hydroxymethyl)furfural (Sigma-Aldrich W501808), glycolaldehyde (Sigma-Aldrich G6805), acetic acid (Sigma-Aldrich 320,099), 1,6-anhydro-β-D-glucose/levoglucosan (Sigma-Aldrich 316,555), and trans-3,5-dimethoxy-4-cinnamaldehyde-(Sigma-Aldrich 382,159). Different dilutions

were prepared until the amounts of standards added were similar and representative for pyrolysis bio-oil samples.

The gas chromatography mass spectrometer (GC–MS) Agilent 5977 series single quadrupole mass selective detector (MSD) was employed for this analysis. The m/*z* range selected was from 29 to 400. Ionization of samples occurs in the 70 eV ion source and the column employed was DB-1701, a low/mid-polarity with 60 m × 250 µm × 0.25 µm stationary phase thickness. Injection was in splitless mode with helium as carrier gas with a flow of 1.2 mL/min. The GC oven was heated from 50 °C (hold for 2 min) to 280 °C at 6 °C/min, held for 16 min.

Compound identification was performed by comparing the m/*z* generated by the GC–MS with the National Institute of Standards and Technology (NIST) library, version 14, examples of compounds identified can be found in Appendix A. Quantification consisted of the area under each peak detected in the chromatogram based on method 8270E from the United States Environmental Protection Agency (EPA) [36] using response factors.

Water content in bio-oil The Dean-Stark method was employed to determine the level of water formed in slow pyrolysis produced bio-oil with ASTM D95 standard method [37].

Water content in bio-oil produced from fast pyrolysis was determined with Karl Fischer titration by VTT described in more details at Oasmaa et al. [38]

Gas. The gas samples from slow pyrolysis were collected directly in Tedlar® PVDF bags. Method developed by Uguna et al. [39] was implemented in a Clarus 580 GC fitted with a flame ionization detector (FID) and thermal conductivity detector (TCD) using an alumina fused silica 30 m × 0.32 mm × 10 µm column with helium as carrier gas. Hydrocarbon (C1-C5) and non-hydrocarbon (CO, CO_2, H_2) gas standards were injected individually to calculate the proportion in the gas sample according to the ASTM D7833-14 standard [40].

2.3 Pyrolysis systems

2.3.1 Slow pyrolysis

This system consisted of a horizontal single-zone Gray King tube furnace with a Carbolite™ controller. A quartz tube (length: 300 mm, inner diameter: 200 mm) was used as the reactor to hold the biomass during pyrolysis. 5–10 g of dry biomass were placed in the quartz tube. This samples were used without any modification or alteration to the structure of the raw material collected directly from the AD system. The moisture content was measured before each experiment to differentiate this water from that one produced in pyrolysis. The reactor was flushed with nitrogen (N_2) to remove traces of air inside the system to enable the experiments to run in absence of oxygen. A difference of +/− 5 °C was detected between the temperature inside of the reactor and the setpoint, with a thermocouple placed inside the reactor. Runs were performed in triplicate at four different temperatures (355 °C, 425 °C, 485 °C, and 530 °C) with a residence time of 30 min. The resulting biochar was contained within the tube. Condensable and non-condensable gases went through a vacuum trap placed in an ice bath in order to recover bio-oil by condensation. Incondensable gas was collected in a sampling bag. The slow pyrolysis apparatus used to process crop digestate is as shown in Fig. 1.

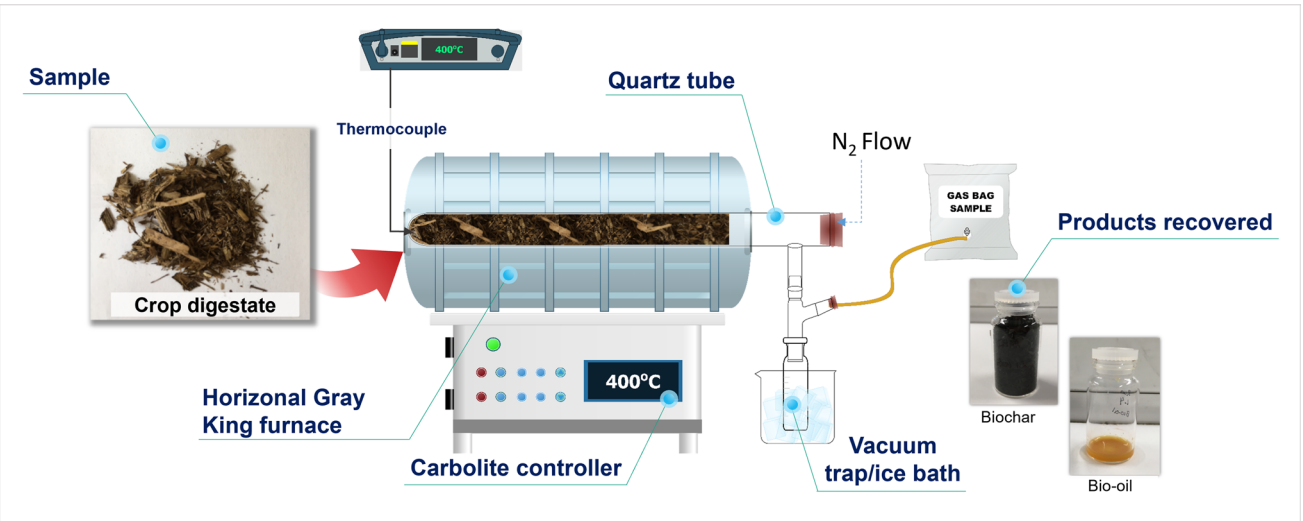

Fig. 1 Slow pyrolysis system employed to process crop digestate at the University of Nottingham

Details about the mass balance equations employed for slow pyrolysis system can be found in Appendix A.

2.3.2 Fast pyrolysis

Crop digestate was processed in a 1 kg/h bench scale unit at the Technical Research Centre of Finland, VTT. The system consisted of a fluidized bed reactor, where approximately 300 g of aluminum oxide (Al_2O_3) was used as fluidizing agent to avoid accumulation of the biochar formed across the reactor [41] and N_2 as an inert gas with a flow around 30 L/min. Residence time of the gas phase is less than one 1 s.

The system requires feedstock with low water content, < 10% wt, and particle size less than 1 mm. Crop digestate had to be pre-treated at VTT, where it went from dry raw material into pellets to be ground, and then sieved to get particle sizes between 0.5 and 0.9 mm. According to Meier et al. [42] maximum yields of bio-oil are generated between 480 and 520 °C. The experiments for this study were carried out at 460 °C, 480 °C, 520 °C, and 560 °C. Moisture content in digestate was measured before every run to quantify and differentiate it from the water produced in lignocellulose decomposition. Each run duration was 3 h to allow the system to stabilize and to obtain a reliable overall mass balance and product recovery for the system.

Biochar was separated from gases and recovered through two cyclones. Hot gases, condensable and non-condensable, went through a liquid recovery section, in which bio-oil was condensed into four fractions. The first section was a water scrubber at around 45 °C where most of the easy condensable gases and water vapor were recovered. The second fraction was for heavier bio-oil compounds which were collected through an electrostatic precipitator. The third and fourth fraction were lighter organics and possible remaining water recovered by glycol coolers. Non-condensable gases were analyzed at the end of the system by directly injecting into a CP-4900 Micro Gas Chromatograph (Varian).

The general diagram of the process of fast pyrolysis set at VTT is shown in Fig. 2.

More detail about the system can be found in Oasmaa et al. [43] and other publications from VTT [44].

2.3.3 Microwave pyrolysis

Crop digestate had a low volumetric density compared with woody biomass. The volume this biomass occupies without pelletizing is greater than that occupied by the reactor vessel in the microwave cavity used for this study. As a result, a manual 24-tonne bench top pellet press (Carver Standard) was employed to densify these biomasses. Around 6 g of ground sample was loaded in a 25 mm-diameter die to obtain a 10 mm long pellet under 10 tons of pressure. This procedure was carried out based on other experiments performed by Kostas et al. [45, 46] using non-woody biomass with low volumetric density and with a moisture content lower than 10% wt in the same apparatus at the University of Nottingham.

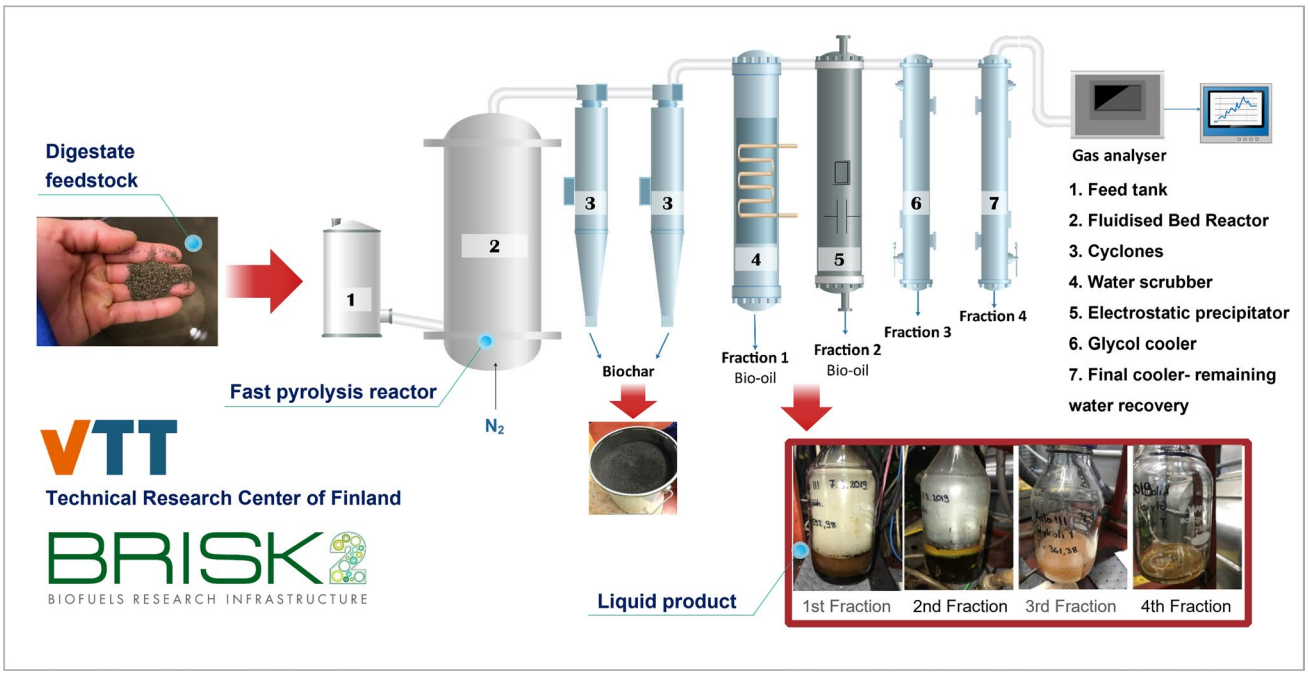

Fig. 2 General diagram of fast pyrolysis system at VTT using crop digestate

This system comprises a 2.45-GHz generator (Sairem, Décines-Charpieu, France) with a maximum power input of 2 kW. This power was delivered to the applicator through a standard WR340 waveguide. To improve the microwave power absorption efficiency, a sliding short-circuit and a three-stub motorized Homer tuner (STHT 2.45 GHz, S-TEAM, Bratislava, Slovakia) were used for impedance matching. The analyzer software within the Homer tuner processes the microwave power signal to obtain absorbed and reflected power profiles.

A 30 mm internal diameter quartz tube was employed as reactor to hold the biomass pellet and placed in a single-mode cavity. N_2 was used as inert gas to run the experiments in absence of oxygen with a flow rate around 2 L/min, controlled with a flowmeter. An inlet line was connected on the top of the reactor to recover condensable gases through two vacuum traps in ice bath allocated at the bottom of the system.

For these experiments the power delivered by the microwave generator was set at 500 or 700 Watts (W). Bio-oil production from digestate with microwave pyrolysis was explored by varying this power input. The output power was absorbed by the biomass or reflected, with reflected power logged over the duration of each experiment and used to calculate the net energy input. Due to the difficulty of measuring the exact temperature inside the system and the biomass, specific energy input (kJ/g) was instead used to present the results of microwave pyrolysis of digestate. This energy is the average power absorbed divided by the time for which initial weighed digestate (g) was pyrolyzed. Only the bio-oil was recovered and analyzed for this system, gas was not collected. The set-up of the microwave system is shown in Fig. 3.

A summary of the main conditions of three pyrolysis systems is shown in Table 1.

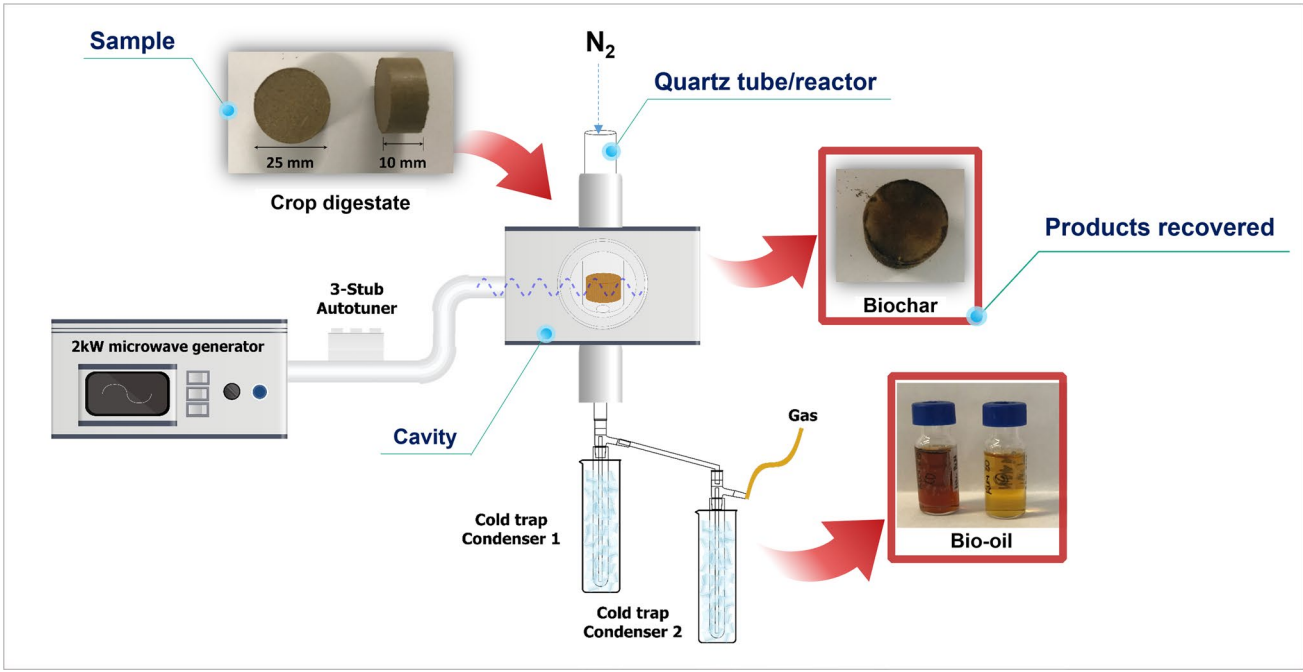

Fig. 3 Microwave pyrolysis system to process crop digestate

Table 1 Summary of main parameters implemented for each pyrolysis system

Parameter	Slow pyrolysis				Fast pyrolysis				Microwave pyrolysis	
Digestate moisture % wt	~4				~4				~4 and ~8	
Particle size/pellet	Raw material no pre-treatment				0.5-0.9 mm				25mm D x 10mm H pellet	
Retention time	30 min				<1s				5 min	
Biomass sample	5-10 g				3-4 kg				~6 g	
Operating temperature, °C	355	425	485	530	460	480	520	560	-	-
Power input, W	-				-				500, 700	

3 Results and discussion

3.1 Properties of feedstock

Samples of crop digestate were collected across a year in order to verify if there was any considerable variability through the seasons. Proximate, ultimate, and lignocellulose analyses results of each collection are presented in Table 2, which also includes the original moisture content measured when the samples were collected direct from the AD system as part of sample preparation described in Section 2.1.

There is a clear similarity between digestate batches in terms of both volatile matter and fixed carbon content; however, it was found to have a great variation in ash content in each sample loaded for the TGA analysis. These differences were detected within the same batch, varying sometimes from 6 to 11% wt, and others reaching higher than 12% wt; some examples of this variation are presented in the supplementary data (Appendix A). The results presented in Table 2 for ash are the average of around six measurements carried out of each batch to obtain a consistency.

The whole digestate collected had the same amount of lignocellulosic material. Cellulose content was found in a range of 23–25% wt, hemicellulose in 19–21% wt, and lignin around 24% wt. Only batches 1–3 were mixed to be processed through the pyrolysis systems, obtained an average amount of ash content of around 9% wt.

3.2 Slow pyrolysis products from digestate

The yields of products recovered from slow pyrolysis of digestate are shown in Table 3.

Closure balance of this system is around 94% wt based on product recovery which is acceptable for this small-scale pyrolysis apparatus. Table 3 results can represent an approach of the amount of water and organics contained in the pyrolytic liquid formed from this type of digestate. Some of the results at the same conditions showed significant differences. This could be caused by variation in ash amount within each sample loaded, and similar behavior was detected in TGA analysis shown in Table 2. As a result, the ash content of the digestate within this technology has a direct impact on pyrolysis product yield and composition.

The highest amount of biochar produced is at 355 °C with 57.34% wt of total products. As the temperature increases,

Table 2 Proximate, ultimate, and lignocellulose analysis of every batch of digestate collected during the seasons within a year.

Parameter	CROP DIGESTATE					
	Autumn		Winter	Spring	Summer	
	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6
Initial moisture	80.86 ± 0.16	81.50 ± 0.184	81.97 ± 0.43	81.13 ± 0.6	79.65 ± 0	78.28 ± 0.01
Proximate analysis						
Moisture	5.07 ± 0.27	4.74 ± 0.41	3.80 ± 1.19	3.8 ± 1.19	4.02 ± 0.17	4.28 ± 0.5
Volatile matter	68.32 ± 1.28	66.96 ± 0.64	65.21 ± 1.64	67.8 ± 0.91	68.51 ± 0.47	67.24 ± 0.59
Fixed carbon	19.30 ± 0.56	19.83 ± 0.50	19.29 ± 0.79	19.02 ± 0.19	19.02 ± 0.19	20.02 ± 0.21
Ash	7.32 ± 1.27	8.48 ± 1.47	11.10 ± 2.49	9.38 ± 0.65	8.43 ± 0.56	8.44 ± 0.84
Ultimate analysis						
C	44.22 ± 0.21	43.86 ± 0.89	44.35 ± 0.66	44.02 ± 0.2	43.84 ± 0.09	43.78 ± 0.12
H	5.74 ± 0.05	5.68 ± 0.13	5.65 ± 0.07	5.85 ± 0.05	5.74 ± 0	5.66 ± 0.03
N	1.52 ± 0.13	1.70 ± 0.03	1.77 ± 0.22	2.01 ± 0.02	1.88 ± 0.01	1.99 ± 0.03
O*	48.52 ± 0.16	48.76 ± 1.04	48.24 ± 0.51	48.12 ± 0.17	48.54 ± 0.08	48.56 ± 0.14
Lignocellulosic material						
Cellulose	24.86 ± 0.06	23.34 ± 0.37	23.06 ± 0.26	22.00 ± 0.43	24.42 ± 0.09	23.95 ± 0.39
Hemicellulose	20.86 ± 0.11	19.38 ± 0.54	19.88 ± 0.15	19.04 ± 0.64	19.84 ± 0.02	19.93 ± 0.28
Lignin**	24.20 ± 2.19	23.80 ± 0.28	24.34 ± 1.38	21.87 ± 0.24	22.89 ± 0.38	23.12 ± 0.45

Data is the mean ± SD, % weight basis, with at least duplicate measurements. *Oxygen was obtained by difference. Cellulose is glucose. Hemicellulose is the combination of xylose, arabinose, and galactose. **Lignin-remaining content of dry matter after subtraction of carbohydrates

Table 3 Yields of slow pyrolysis products carried out at four different temperatures using crop digestate feedstock dry basis.

Slow pyrolysis				
Product	355 °C	425 °C	485 °C	530 °C
Biochar	57.34 ± 3.52	45.30 ± 0.72	41.18 ± 1.05	39.63 ± 1.80
Bio-oil	31.45 ± 3.62	42.19 ± 1.94	45.13 ± 1.42	46.02 ± 1.11
Organics	18.98 ± 4.72	26.26 ± 2.61	26.68 ± 2.13	27.02 ± 1.58
Water	12.47 ± 3.46	15.93 ± 0.91	18.45 ± 0.80	19.01 ± 0.60
Gas	4.10 ± 1.59	5.32 ± 1.17	8.30 ± 1.06	9.19 ± 2.06
Total products	95.41	92.81	94.61	94.84

Data is the mean ± SD, % weight basis, with at least duplicate measurements

biochar yield is reduced. If the aim of thermochemical conversion of biomass is to obtain high biochar yields, slow pyrolysis at temperatures lower than 400 °C could be optimum to achieve this. The variation in slow pyrolysis product yields between 355 °C and the other temperatures is noticeable. The water is proportionally highest at 355 °C, almost comprising 50% wt of the total liquid. This increased by around 30% wt between 355 and 425 °C and by 15% wt between 425 and 485 °C. Organics showed a 40% increase from 355 to 425 °C, after which there was little change. The amount of organics produced between 425 and 530 °C remained very similar in proportion, with around 27% wt. Gas and biochar require further analysis and evaluation for further uses; however, these are not within the scope of this study.

3.3 Fast pyrolysis products from digestate

The general distribution of fast pyrolysis products recovered from digestate at different temperatures are shown in Fig. 4. The data comprises water and organics, similar to the data presented for slow pyrolysis.

The total mass balances in the experiments were around 90% wt which is consistent with the system product recovery presented by Oasmaa et al. [43], and Lindfors et al. [47].

Due to the larger mass of biomass tested in this system the products were collected after 3 h of operation. Fast pyrolysis of digestate produced between 7 and 11% wt of water as product, which increased at higher temperature, above 500 °C. The maximum amount of water quantified from this system is much less than that produced in slow pyrolysis. Organics, however, were relatively constant through the experiments. There was an increase observed at 480 °C, whereas at 460 °C, 520 °C, and 560 °C organics were produced at around 30% wt. The lowest gas generation was around 18% wt at 480 °C, with a slight increase through other conditions to reach a maximum production of just above 20% wt at 560 °C. Biochar product from digestate in this pyrolysis was less than 35% wt in all the experiments. This was different to the biochar generated in slow pyrolysis, where it was at least 40% wt of the total products.

Fast pyrolysis products of digestate were generated at similar proportions in each processing condition. However, it was important to identify any possible variation in product composition and the differences between them occurring with temperature changes and evaluate the quality of the pyrolytic products.

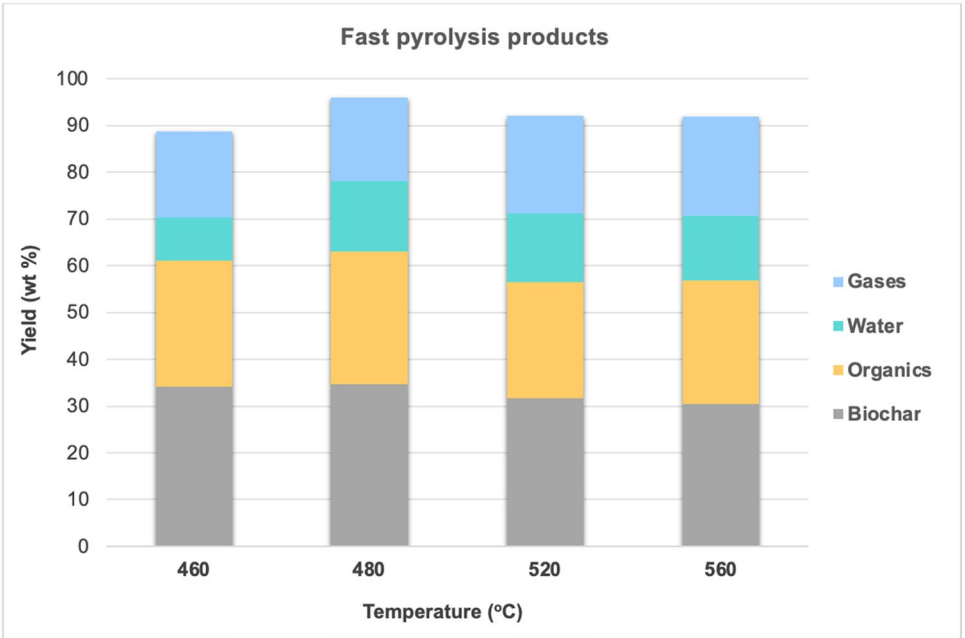

Fig. 4 Yields of fast pyrolysis products recovered at different temperatures from digestate

3.4 Properties of products

3.4.1 Gas

Gases collected from these systems consist of large amounts of carbon monoxide (CO) and carbon dioxide (CO_2). These represent 16–19% wt of the total products in fast pyrolysis of digestate, and between 4 and 10% wt in slow pyrolysis. More details of the average amount quantified at each operating conditions for slow and fast pyrolysis can be found in Appendix A. Hydrogen and methane were detected in the gas produced from both technologies, but these reached a production less than 1% wt in total at the highest temperatures. There was also a variation between concentration in gas samples at the same conditions. These differences could be due to ash content in each set of experiments where some degradation or further reactions might occur and some of the larger compounds could break down into small molecules and leading these two gases increasing their generation.

3.4.2 Bio-oil

All the compounds found in the bio-oil recovered were categorized into seven chemical groups: acids, aldehydes and ketones, alcohols, furans, sugars, phenolics, and the rest as others.

Bio-oil analysis was the key for this study in understanding more about each thermochemical process and the behavior of digestate during pyrolysis. Every bio-oil presented great difference in composition, including the samples obtained at the same condition. As a result, each experiment performed was considered independent test due to possible variation of ash in each sample loaded in the reactor which is directly related with chemical composition determined in the bio-oils.

Slow pyrolysis Two examples of bio-oil analysis of each set of experiments are shown in Table 4. The analysis presented is based on the whole liquid recovered from pyrolyzing digestate, which includes organics and water produced during pyrolysis. The variability in yields highlighted in Section 3.2 also occurred in bio-oil chemical composition.

The lowest yield of bio-oil was at the lowest temperature, in this case 355 °C, but there was a high content of acids. As temperature increased the concentration of acids generally reduced. Total acids not only varied in each bio-oil across temperatures, but also in those resulted from experiments carried out at the same conditions. At 355 °C for instance, acid production was 9.62% wt in run 1 whereas 11.18% wt of acids were formed in run 2, besides other samples at this temperature resulted with even a larger amount. Another example of a significant variation in acid generation was slow pyrolysis performed at 530 °C, where run 1 resulted with 8.61% wt acids while run 2 had only 1.80% wt. This could result from different ash content in each sample loaded for the experiments.

Phenolics had a different trend from acids, their concentration increased with increasing temperature. The amount of these compounds produced went from 10–12% wt at 355 °C to almost 30% wt at 530 °C. This is likely to be associated with lignin decomposition, which requires more energy and higher temperatures to be depolymerized to form these organics in the liquid product [48, 49].

Fast pyrolysis Bio-oil resulting from the fast pyrolysis system was examined with the same method by which slow pyrolysis bio-oil was processed. The summary of this analysis is shown in Table 5 and which shows bio-oil quantification by chemical groups at different temperatures.

Sugars were identified in these bio-oil samples at around 1–3% wt, and very small amount of alcohols, less than 1% wt. Additionally, there was less acid production at the lowest and highest temperature. Phenolics were formed at relative high proportion in most of the temperatures at

Table 4 Proportions of chemical groups in slow pyrolysis bio-oil of digestate. Data is presented in % weight basis, and total bio-oil represents yields

Slow pyrolysis bio-oil								
Groups	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
	355 °C	355 °C	425 °C	425 °C	485 °C	485 °C	530 °C	530 °C
Acids	9.62	11.18	8.57	6.00	2.67	2.80	8.61	1.80
Aldehydes and ketones	3.13	4.66	4.47	3.95	3.60	3.10	3.62	2.14
Alcohols	2.38	0	0	0.11	0	0	0	0
Furans	3.50	5.37	6.22	7.53	9.78	9.60	6.79	13.12
Sugars	0.14	0.20	0.50	0.46	0.21	0.21	0.55	0.08
Phenolics	9.63	12.32	18.82	21.33	27.01	25.44	22.79	28.37
Others	2.22	1.67	3.02	2.65	3.10	2.44	2.40	0.92
Total bio-oil	30.63	35.40	41.59	42.04	46.36	43.58	44.77	46.43

Table 5 General composition of bio-oil produced from fast pyrolysis of digestate. Data is presented in wt % and total bio-oil represents yields

Fast pyrolysis bio-oil				
Groups	460 °C	480 °C	520 °C	560 °C
Acids	6.20	23.49	13.45	6.64
Aldehydes and ketones	4.03	4.25	3.76	4.41
Alcohols	0.17	0.68	0.44	0.43
Furans	3.46	2.54	3.41	6.31
Sugars	1.28	3.31	2.12	1.86
Phenolics	19.00	7.53	14.43	17.62
Others	1.90	1.70	1.85	2.88
Total bio-oil	36.03	43.50	39.48	40.15

14–19% wt, only at 480 °C it was much lower. These phenolics at 480 °C could be decomposed into other smaller molecules because the biomass had to be ground prior to pelletization. This could lead to lignin to being decomposed more easily, and the amount of energy employed could result in a surplus which was then able to break down phenolics into smaller molecules. Ash could have played a catalytic role in this further decomposition into other chemicals to form more acids. Aldehydes and ketones were at low concentration in most of these conditions, very similar to slow pyrolysis yields. Furans, however, are at smaller amounts with a maximum of approximately 6% wt, whereas in slow pyrolysis, they reached to around 13% wt at 530 °C.

Microwave pyrolysis The dry digestate employed in this research is not a good absorbent microwave material. Energy absorbed in each experiment was only around 100 W out of 500 W, and 700 W. Samples with higher moisture content presented different composition from the dry digestate. Six examples of bio-oils recovered from this technology are presented in Table 6.

Experiments with specific energy input of 1.27 kJ/g and 1.88 kJ/g, for instance, were performed at the same power input, 700 W, and bio-oil yields and compositions were different. Production of aldehydes and ketones and phenolics was higher at 1.88 kJ/g with almost 6% and 7% wt respectively, but with a lower concentration of furans. Bio-oil resulting from 1.27 kJ/g energy input contained some alcohols and sugars, whereas these were not detected at 1.88 kJ/g. Additionally, grinding of digestate could have caused a higher ash surface area to be distributed through the samples due to small stones found in digestate. It was also expected that more sugars could be formed from cellulose and hemicellulose using microwaves compared with conventional pyrolysis. Both polysaccharides could be converted into sugars and furans, such as furfural, when subjected to a thermochemical process, yet this was not the case. Large amounts of levoglucosan, product from cellulose, have found when biomass such as wood is thermal treated with microwave pyrolysis [50], different from these microwave experiments using crop digestate.

Biomass conditions in two runs, 4.07 kJ/g and 5.08 kJ/g, were modified. Dielectric properties of these samples were increased by adding some water, which increased microwave interaction with digestate. Digestate considered "dry" contained approximately 4% moisture, and samples with additional water reached around 8% wt moisture. Previous research shows that water content in biomass could lead to more bio-oil and gas production [51–53] which was important to consider for this analysis.

The first comparison between bio-oils from dry and wet biomass was samples with an energy input of 4.07 kJ/g (Table 6). Although this number is the same in both cases, the tests were performed at different power input. The experiment which resulted in a yield of around 18% wt was performed using a digestate sample with a moisture content of 7.34% wt, and power input of 500 W. The other test with bio-oil yield resulting in around 20% wt was conducted with a sample with approximately 4% wt of moisture and using

Table 6 Bio-oil composition of microwave pyrolysis of digestate (wt %) at different energy inputs

Microwave pyrolysis bio-oil						
Groups	1.27 kJ/g	1.88 kJ/g	4.07 kJ/g	4.07 kJ/g	5.08 kJ/g	6.85 kJ/g
	Dry	Dry	Wet	Dry	Wet	Dry
Acids	3.48	4.70	3.51	7.89	3.90	6.27
Aldehydes and ketones	3.37	5.95	3.72	5.33	1.20	1.69
Alcohols	0.05	0.00	0	0	0.02	0.02
Furans	2.98	2.44	3.50	2.76	0.70	3.13
Sugars	0.06	0.02	0	0	0.07	0
Phenolics	5.43	6.85	6.90	4.28	6.10	3.90
Others	0.94	0.70	0.73	0.60	2.41	1.07
Total bio-oil	16.30	20.65	18.35	20.86	14.40	16.08

a power input of 700 W. Although, lignin is one composite of lignocellulosic material that requires more energy to be decomposed [19, 20], the amount of produced phenolics indicates that larger amount of lignin could be depolymerized with microwave pyrolysis because of that additional water. Therefore, more phenolics were obtained with higher moisture using lower power: 500 W resulted in almost 7% wt, in contrast to around 4% wt obtained using 700 W.

Similar behavior was detected for samples with energy input of 5.08 kJ/g and 6.85 kJ/g, utilizing digestate with almost 10% and 4% of moisture and conducted at different power input, 500 W and 700 W, respectively. Both cases showed bio-oil from wet digestate contained more larger molecules and less acids, and this is an evident difference with the other bio-oils from dry digestate. Robinson et al. [54] presented studies of cellulose and hemicellulose decomposition using microwave pyrolysis, where one of the variables studied was water content. These results revealed that higher moisture content can lead to the depolymerization of cellulose and hemicellulose to form larger amount of levoglucosan and furfural at lower temperatures. This mechanism has similarities to what occurs during hydrothermal decomposition of lignocellulosic material, and the same outcomes could have arisen when digestate was subjected to microwave pyrolysis due to the amount of cellulose and hemicellulose within this material. However, ash content in this biomass led to lower yields of these products in the liquid, although the energy input and ash could have enhanced the depolymerization of lignin.

Bio-oil comparison An illustration of the distribution and variation of bio-oil compositions from the three pyrolysis technologies are shown in Fig. 5.

Alcohols and sugars were barely formed from crop digestate using slow pyrolysis (Fig. 5A). The maximum alcohol yield was around 2% wt at 355 °C, a very small amount was formed at 425 °C with only 0.1%, and no formation was observed at 485 °C and 530 °C. Sugars were detected across the operating temperatures; however, they were at very low concentration. The range of sugar production was only between 0.1 and 0.55% wt. Aldehydes and ketones were formed almost at the same proportion in most of experiments, between 2 and 5% wt, but furans were at variable concentration among all the slow pyrolysis bio-oils across these temperatures, with the highest quantity at 530 °C.

Sugars were found in a greater amount in fast pyrolysis bio-oil (Fig. 5B), whereas in slow bio-oil they did not even reach 1% wt. Some alcohols were detected in most of the samples from fast pyrolysis, and only one sample in slow pyrolysis contained these. It is evident that the composition and distribution of these chemical groups varied between these two pyrolysis bio-oil.

Acid content was high in most of microwave pyrolysis bio-oils (Fig. 5C). Sugars and alcohols were detected in low concentration in few samples with less than 1% wt. Aldehydes and ketones in some cases reached yields considerably higher than those from slow and fast pyrolysis, where the highest amount was under 5% wt. This technology produced in a few bio-oil samples almost 6% wt of these compounds; digestate pyrolyzed with 1.88 kJ/g energy input for instance.

The amount of furans was relatively consistent across these systems, with only one low value, less than 1% wt, from microwave pyrolysis at 5.08 kJ/g energy input, whereas the lowest amount generated in fast pyrolysis was 3.46% wt at 460 °C and 3.5% wt in slow pyrolysis at 355 °C. Aldehyde and ketone production decreased with slow and microwave pyrolysis at higher temperature and energy input. There was just a minor increase of these in fast pyrolysis from 4.03 to 4.41% wt. Phenolics were formed in the highest proportion across these technologies. There was an increase of these in slow from around 9% to almost 23% wt, a variation in microwave between 4 and 7% across the energy input. Contrastingly, these were slightly less generated in fast pyrolysis, reduced from 19% wt at 460 °C to 17.82% wt at 560 °C.

Composition of bio-oils from digestate treated using the three pyrolysis technologies is compared in Table 7. Samples obtained under equivalent conditions of temperature or energy input were selected to be evaluated. In the range of conditions implemented to pyrolyze crop digestate, medium and high values of specific energy input and temperature were considered for this analysis. Only bio-oil was selected for this comparison due to the range of chemicals can be found in. Some of these compounds are derived from cellulose, hemicellulose, and lignin, and could give indications of the decomposition of lignocellulose in digestate occurs through these technologies.

The first highlights are the production of levoglucosan only in fast pyrolysis at 460 °C, and 560 °C and the lowest amount of acetic acid in microwave pyrolysis using wet digestate with around 3% wt, whereas in the other technologies, the amount of this acid was between 4.5% wt and almost 8% wt.

Furfural, one of the most common primary compounds formed from lignocellulosic material could have been generated but transformed into other smaller molecules. According to mechanisms in the literature, bio-oil compounds expected might have been decomposed into smaller molecules such as furan,3-methyl-, 2-furanmethanol, butyrolactone, 2-furanmethanol, tetrahydro- and 2-cyclopenten-1-one [55, 56], if secondary reactions took place, and the presence of these in most of the bio-oils recovered suggests that this might have occurred during pyrolysis of digestate.

Lignin derivatives such as phenol were generated in greater proportion at high temperatures in slow and fast

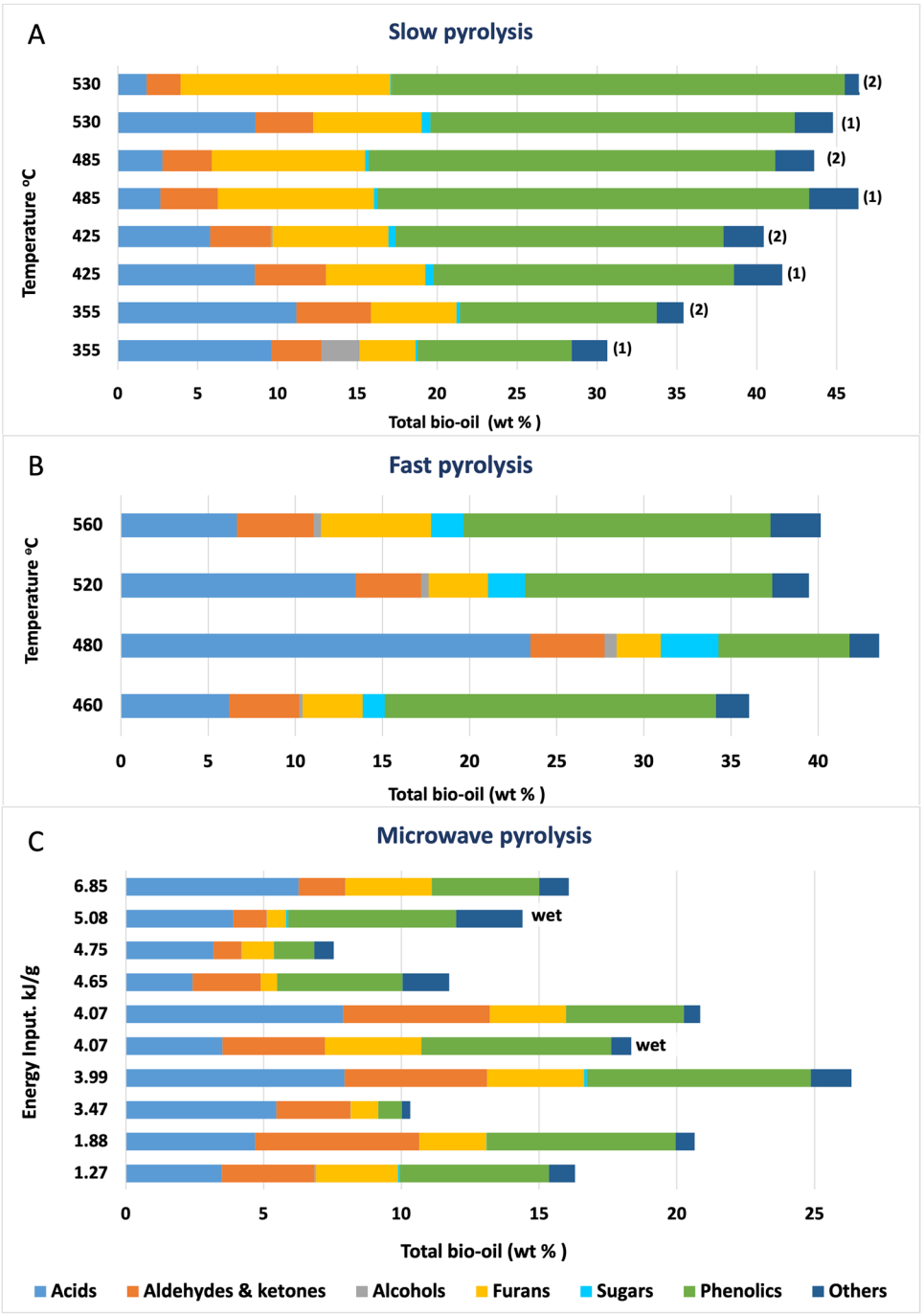

Fig. 5 Mass weight distribution of the chemical groups found in bio-oils from digestate across the three technologies: **A**) slow pyrolysis, **B**) fast pyrolysis, and **C**) microwave pyrolysis

pyrolysis in around 2–4% wt. The largest amount of syringol was found in slow pyrolysis with a minimum of 4% wt. 2-Methoxy-4-vinylphenol was identified in most of the bio-oils, but the largest amount quantified was in slow pyrolysis at 530 °C with 2.32% wt. Another compound formed in high proportion was benzofuran, higher than 4% wt in slow and fast pyrolysis at 530 °C and 560 °C. All these compounds have been identified as high value derivative from lignin for further uses in the industry to produce biopolymers, foams, or other biobased chemicals [57, 58].

The primary limitation of this study is that it was not been possible to make a direct and meticulous comparison between these three pyrolysis technologies due to some operating parameters, for instance energy input and temperature. It is complicated to measure the temperature in the microwave system to interpret how the lignocellulose

Table 7 Bio-oil comparison between the three pyrolysis technologies from digestate. Proportions of chemical groups are presented in % wt of the total bio-oil of one experiment at certain conditions: temperature or specific energy input

GROUPS	Medium			High			
	Slow 425°C Dry	Fast 460°C Dry	Microwave 1.88 kJ/g Dry	Slow 530°C Dry	Fast 560°C Dry	Microwave 3.99 kJ/g Dry	Microwave 4.07 kJ/g Wet
ACIDS							
Acetic acid	7.5	5.7	4.5	7.9	6.1	7.4	3.13
Propanoic acid	0.7	0.5	0.2	0.7	0.6	0.5	0
ALDEHYDES & KETONES							
2-Propanone, 1-hydroxy-/Acetol	0	0	3.18	0	0	2.71	0.94
Acetoin	0	0	0.09	0	0	0	0
1-Hydroxy-2-butanone	0.08	0	0.48	0	0	0.61	0.52
2-Cyclopenten-1-one	0.15	0.18	0.66	0.28	0	0.58	0.62
2-Propanone, 1-(acetyloxy)-	0.36	0.34	0.26	0.47	0.30	0.27	0.34
2-Cyclopenten-1-one, 2-methyl-	0.11	0.36	0.23	0.34	0.56	0.18	0.18
2-Cyclopenten-1-one, 3-methyl-	0	0.71	0.19	0	1.00	0	0
1,2-Cyclopentanedione, 3-methyl-	0.84	0	0.61	1.58	1.77	0.58	0.65
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0	1.76	0	0	0	0	0
1,3-Cyclopentanedione, 2,4-dimethyl-	0	0.18	0	0	0.24	0	0
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.36	0.49	0.16	0.53	0.29	0.18	0.17
4-Hexen-3-one, 4,5-dimethyl-	0.16	0	0.04	0.19	0	0	0.08
ALCOHOLS							
Cyclohexanol, 4-methyl-, cis-	1.03	0	0	0	0	0	0
Cyclohexanol, 4-methyl-	0.98	0	0	0	0	0	0
3-Hexanol, 5-methyl-	0.08	0	0	0	0	0	0
1-Octanol, 2-butyl-	0.16	0	0	0	0	0	0
FURANS							
Furfural	0	0	0	0	0	0	0
Furan, 3-methyl-	0	0	0	0	0.24	0	0
2-Furanmethanol	0.70	0.38	0.51	0.52	0.40	0.87	0.9
Ethanone, 1-(2-furanyl)-	0.20	0	0.03	0	0	0.09	0.08
Butyrolactone	1.16	0	0.19	1.01	0	0.53	0.58
2-Furanmethanol, tetrahydro-	0.66	0	0.08	0.44	0	0.17	0.17
2(5H)-Furanone	0	0	0.04	0	0	0	0.09
Benzofuran, 2,3-dihydro-	2.97	2.86	1.47	4.36	5.48	1.74	1.60
5-Hydroxymethyldihydrofuran-2-one	0.30	0.22	0.07	0.33	0.18	0.08	0
SUGAR							
1,4:3,6-Dianhydro-.alpha.-D-glucopyranose	0.25	0.16	0.02	0.19	0.31	0.02	0
DL-Xylose	0.23	0.34	0	0.36	0.36	0.08	0
D-Mannose	0	0.24	0	0	0.35	0	0
β.-D-Glucopyranose, 1,6-anhydro-/levoglucosan	0	0.54	0	0	0.84	0	0
PHENOLICS							
Phenol	1.77	1.68	0.71	2.49	4.03	0.63	0.74
Phenol, 2-methoxy-	5.30	2.90	1.49	5.46	1.78	1.74	2.48
Phenol, 2-methyl-	0.26	0.54	0.17	0.62	1.03	0.10	0.08
p-Cresol	0.45	0.90	0.16	0.90	0.95	0.04	0.12
Creosol	1.75	0.86	0.52	1.60	0.49	0.44	0.25
Phenol, 3,5-dimethyl-	0	0	0.04	0	0.48	0	0
Phenol, 2,3-dimethyl-	0	0.32	0	0	0.12	0	0
Phenol, 4-ethyl-	0.61	2.21	0.34	0.89	2.79	0.37	0.32
Phenol, 4-ethyl-2-methoxy-	0	1.15	0.58	0	0.43	1.12	0
2-Methoxy-4-vinylphenol	1.64	1.58	0.90	2.32	0.88	1.29	1.36
Eugenol	0	0.21	0	0	0.30	0	0
Phenol, 2,6-dimethoxy- / Syringol	4.35	3.01	0.98	5.84	0.98	1.21	0.91
Phenol, 2-methoxy-4-(1-propenyl)-/Isoeugenol	0.15	0.24	0	0	0	0.02	0
trans-Isoeugenol	0.39	0.84	0.16	0.55	0.46	0.17	0.13
3,5-Dimethoxy-4-hydroxytoluene	0.48	0.52	0.15	0.54	0.27	0.17	0.08
Vanillin	0	0	0	0	0	0.03	0.05
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.29	0.25	0.10	0.34	0	0.12	0.07
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0	0	0	0	0.19	0.05	0.05
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	0.24	0.25	0.04	0.27	0	0.04	0.05
2-Pentanone, 1-(2,4,6-trihydroxyphenyl)	0.28	0.14	0.04	0.21	0.16	0.04	0.05

is decomposed in this specific waste, and how other compounds can be formed by secondary reactions taking place. It was crucial to understand why during the thermochemical decomposition of lignocellulosic material furfural and sugar such as levoglucosan were not formed as expected. There have been studies of this technology in pyrolyzing woody material and due to microwave mechanism high yield of furfural and levoglucosan has resulted, yet with "cleaner" wood than digestate with under 1% wt of ash [50, 59]. The heating mechanism in microwave and the ash distribution could also lead to breaking down some primary organics formed from lignocellulose. This can be represented in Fig. 6.

Results from microwave pyrolysis of digestate where the experiments were carried out with wet biomass were favorable for lignin when it is decomposed in presence of ash, resulting in larger amount of phenolics in the bio-oils. Slow pyrolysis of digestate at high temperatures also produced phenolics in high proportion. On the contrary, with fast pyrolysis at 480 °C, acids were in greater proportion than phenolics and this could also be influenced by the feedstock preparation. This and ash content could also lead to the conversion of these lignin-derived products into other compounds, producing smaller molecules such as acetic acid and CO_2.

The digestate used is analyzed regularly at the AD plant by Schmack Biogas Service to determine nutrients within

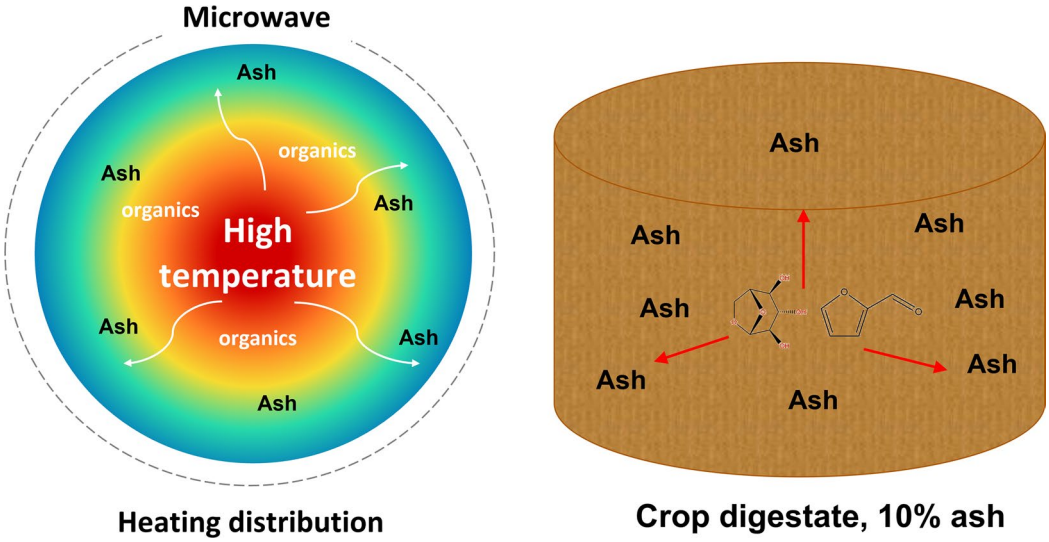

Fig. 6 Illustration of possible effect of ash distribution and microwave mechanism through digestate pellets utilized in microwave pyrolysis. Microwave heating diagram modified from Miura et al. [27]

the material and to determine it is suitability for use as a fertilizer. Some of the inorganic compounds found are calcium, phosphorus, magnesium, and potassium, and also, some metals such as copper and zinc in very low concentration. All these inorganic compounds are considered catalysts in biomass thermochemical processing [60, 61]. Some have analyzed their effect on pyrolysis products formation and composition, where reactions can result in dehydration and lead to more water and CO_2 generation [60–62] which is what may possibly be occurring during pyrolysis processing of crop digestate.

Another limitation in this study that could be addressed in future research is the qualitative and quantitate analysis of the inorganic material in this waste. The analysis of ash content within each sample loaded in the pyrolysis system could reveal in more detail the impact on chemical composition of the pyrolytic products from this lignocellulosic digestate.

4 Conclusions

Although digestate has around 45% wt of holocellulose, the chemical composition of bio-oil indicated that primary compounds experienced secondary reactions through the pyrolysis systems, mainly due to the high acetic acid and low sugar concentration detected. However, large amounts of aldehydes, ketones, and phenolics were found in these bio-oils resulted from these three pyrolysis technologies, which could be used for further green chemical products. The high levels of phenolics in most of the bio-oils suggests lignin decomposition occurs despite high ash content. Alternatively, these compounds could be a target due to their stability at high temperatures when lignin is subjected to this type of thermochemical processing. If pyrolysis is employed to treat this digestate, lignin could be isolated pre-pyrolysis to produce aromatic biochemicals, and holocellulose could be used for other applications.

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Declarations

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

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