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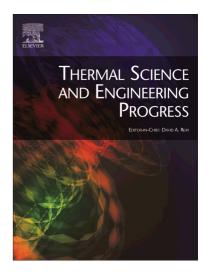
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Experimental investigation on the chemical characterisation of pyrolytic products of discarded food at temperatures up to 300°C

Hussam Jouhara^a, Darem Ahmad^a, Dina Czajczyńska^b, Heba Ghazal^c, Lorna Anguilano^d, Alan Reynolds^d, Piotr Rutkowski^b, Renata Krzyżyńska^b, Evina Katsou^a Stefaan Simons^a, Nik Spencer^e

ABSTRACT

Discarded food generation is one of the most crucial problems of constantly growing modern society. There are several conventional treatment methods of this type of material, however, each one has its own advantages and disadvantages. Pyrolysis, a thermal degradation process, has recently been attracting an increased attention in this field. Pyrolysis allows the utilization of resources to recover the energy within materials with relatively low environmental impact. In this paper results of food pyrolysis products analysis are shown. Liquid and solid residue were tested for the content of various compounds and elements. Composition and concentration of particular compounds and elements indicates a strong presence of long chain alkane and alkene, as well as carboxylic acid molecules within the bio-oil samples. The presence of heavy metals in residues was detected, too. The idea of low-temperature thermal treating in household was critically analyzed. In general, the composition of products from low-temperature slow pyrolysis is safe for the environment. The obtained bio-oils and ash are non-toxic, therefore food residues can be utilized through pyrolysis. The most important advantage of proposed solution is no need of pretreatment of chamber load, and possibility of simple energy recovery for home.

Keywords: Low temperature pyrolysis, Bio-oil, Energy, FT-IR, GC/MS.

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^a College of Engineering, Design and Physical Sciences, Brunel University London, Uxbridge, Middlesex UB8 3PH, UK

^b Faculty of Environmental Engineering, Wroclaw University of Science and Technology, Wyb, Wyspiańskiego 27, Wroclaw, Poland

^c School of Pharmacy and Chemistry, Kingston University, Kingston Upon Thames, KT1 2EE, UK

^d Experimental Techniques Centre, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

^e Manik Ventures Ltd & Mission Resources Limited, Offenham Road, Worcestershire Evesham WR11 8DX, UK

Nomenclature

FAO Food and Agriculture Organization

GHG Greenhouse gases

Gt Gigatonne e Equivalent ha Hectare

FT-IR Fourier-transform Infrared GC/MS Gas chromatography/ mass

spectrometry

m/z Mass-to-charge ratio

RT Retention time

1. Introduction

Discarded food materials are – at the same time – a global problem and a resource with enormous potential. Each year food worth billions of dollars is discarded becoming waste, mainly in the developed countries with the USA as a "leader". In 2014, the Food and Agriculture Organization (FAO) estimated that annually society lost 936 billion USD globally [1]. However, the cost of discarded food is much higher, since the cost of indirect consequences of degraded environmental resources should be included, too. The generation of discarded food materials is going to increase gradually due to economic and population growth mainly in Asian countries [2].

Discarded food materials are defined as any uneaten food or residues from food preparation sourced in residences or commercial establishments and it may be divided into at least two groups. The first group of uneaten food may be avoided (e.g. plate leftovers). The second group consists of plant and animal parts, which are not normally eaten (e.g. peelings, egg shells) [2,3]. The composition of typical uneaten food from households varies significantly depending on its origin. It can be said that animal products are rich in proteins and lipids; fruits, vegetables and grains usually contain a lot of carbohydrates. The elemental composition of proteins, lipids and carbohydrates indicates that a significant amount of carbon is available, thus discarded food is easy to biodegrade [4]. However, it is common that pieces of packaging (plastics, paper, and aluminum foil), paper tissues, toothpicks etc. also appear in the mix of discarded food and impede biodegradation, but this does not contribute to any implications for the thermochemical processes.

In general, discarded food features high concentrations of nutrients, a high calorific value and a high biodegradation rate. That allows it to be utilized by various methods, including composting or animal feed production, heat recovery by different thermochemical processes, and recovery of biogas by anaerobic digestion [5]. Unfortunately, a lot of food still ends up in landfill sites and its potential becomes untapped. Dumping food causes serious environmental problems starting with uncontrolled emissions into air and water, and ending with creating good conditions for pathogen, insect and rodent growth. The environmental impact of throwing away food into landfill sites around the world is shown in Table 1.. As it can be seen from the table, unused food contributes to GHG emissions, soil erosion and

deforestation. Moreover, it occupies almost a million ha of land and causes enormous water contamination. Additionally, many resources are used for transportation and pretreatment of this resource before it reaches its final destination. It is estimated that collection costs vary between 40 and 60% of all of a community's discarded materials management costs [6,7]. Composting and anaerobic digestion can be applied at a domestic level. However, many times they fail and produce more problems than they solve, such as odors [8,9]. Therefore, it is evident that there is an urgent need to find alternative effective ways to cope with biodegradable materials that are produced in households.

Table 1. Main global environmental impact of discarded food [1].

Environmental	Unit	Global
impact		
GHG emissions	Gt CO ₂ e	3.49
Land occupation	Million ha	0.90
Water use	km ³	306
Soil erosion	Gt soil lost	7.31
Deforestation	Million ha	1.82

As mentioned earlier, unused food is a rich source of energy. Therefore, it has a good potential to be a feedstock for thermochemical processes. The advantage of this solution, in comparison with composting and anaerobic digestion, is the independence of sensitive microorganisms and possibility of utilizing all carbon-containing molecules in the raw material instead of their partial accumulation in microbes [10,11]. In general, three types of thermochemical processing of discarded materials may be distinguished: incineration, pyrolysis and gasification. These three treatments methods are the most commonly used to extract the energy held within the raw materials [12]. Each one has important features and they are briefly described below.

Incineration is a process of full oxidation of raw material and sufficient amounts of oxygen must be introduced into the chamber. During the process, the operating temperature of 850°C must be kept for at least 2 seconds (unless the content of halogenated organic substances, expressed as chlorine, does not exceed 1 %) [13]. Incineration plants must be equipped with advanced flue gas cleaning systems in order to prevent uncontrolled emissions. Additionally, solid residues (ash and dust) must be treated in a proper way, since a significant amount of hazardous substances accumulate within them [13].

Gasification is a thermochemical process, which involves partial oxidation under high temperature (usually around 700°C). During gasification, the solid mass of feedstock is converted into gaseous fuel. The solid residue arising has a relatively low carbon content. The composition of gases obtained strongly depends on the type of raw material used in the process, but basically syngas consists of carbon monoxide, hydrogen and methane [12,14]. Since syngas features good properties as a gaseous fuel, the gasification process is usually designed in a way to sustain itself by the gas produced. This makes it quite widely used in the waste management sector.

Pyrolysis is the process of producing pyrolytic oil (a mixture of organic chemicals with water), syngas and biochar [6]. It is a method of thermal decomposition of feedstock that occurs at a high temperature (between 300 and 1000 °C) under atmospheric pressure in the

absence of oxygen. Inert gases, such as nitrogen or argon, are commonly used in the reactor. Vacuum pyrolysis is less popular in practice, since it is generally more complicated [15]. It is possible to select the conditions of the process – especially temperature - in order to obtain the most desirable products. Temperatures below 400 °C result in bulk product volatilization with high formation of a solid char. Higher temperatures (around 500 °C) are desirable when the process aims to mainly produce oil. Finally, when the temperature exceeds 700 °C, large amounts of high quality pyrolytic gas are produced [16]. Pyrolysis has been attracting increased attention in resource-to-energy processes for a long time, because it has very important advantages. Firstly, pyrolysis contributes to the reduction of corrosion and emissions by retaining the majority of metals, sulfur and chlorine within the process. Moreover, the formation of NO_X is also cut due to the relatively low temperatures of the process and reduction atmosphere [6]. Secondly, the scale of pyrolysis plant is more flexible than incineration plants and it is possible to use it even in a household [16]. Finally, pyrolysis allows the transformation of low-energy density discarded materials, such as food, into valuable bio-fuels with high-energy density [17,18].

Pyrolysis of discarded food for the production of fuels [19] and materials [20] has been applied in many previous studies, but the feedstock was in principle sorted, pretreated (shredding, drying) and carefully chosen [21]. Food samples used in pyrolysis reactors in literature are: dog food [11]; cereals [22]; peanut crisps [22]; potato peels [23]; soybean protein [24]; peelings and choppings of various raw vegetables and fruits [25]; mixtures of rice, vegetables and meat/bones [19,26]; and many others. The advantage of this study is the fact that discarded food material was not pretreated in any special way and samples consisted of real food that would otherwise have been discarded from kitchens in UK households. The composition of the bio-oils and solid products obtained is, therefore, very realistic. Additionally, the novel construction of a chamber based on heat pipes [12] was used that allows the pyrolysis of discarded food materials at 300 °C and utilizes unused food as a valuable energy resource.

2. Experimental set-up

The experimental set-up, called HERU (Home Energy Resource Unit [12]), consisted of a reaction chamber which was heated up and maintained at 300 °C using heat pipe technology. The design of HERU's heat pipe based pyrolysis chamber is shown in figure 1. This was achieved using an electronic temperature control unit. The main advantage of using heat pipes is that they have a uniform temperature at any point, which is not the case for any other heating method [27]. This allows the feedstock to be heated at the same temperature at any location within the reaction chamber.

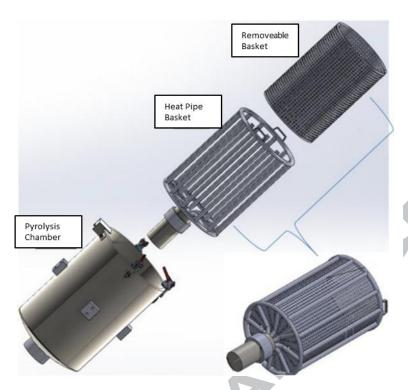


Figure 1. HERU heat pipe pyrolysis chamber.

Thermal insulation was installed at all places where heat could be lost to prevent heat loss to the surroundings. A schematic of the pyrolysis reactor used for this experiment is shown in Figure 2.

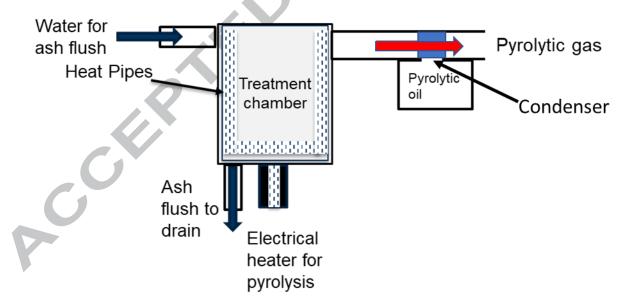


Figure 2. HERU's pyrolysis reactor schematic. The ash is collected through a drain, whilst the pyrolytic vapour produced is condensed in a condenser, resulting in the formation of bio-oil.

The chamber was loaded with various mixtures of food materials. K-type thermocouples were placed in the items of food and in the pyrolysis chamber, as well as the heat pipe legs and the loading basket.

Water based oil was collected once the feedstock was pyrolyzed and then condensed at the heat exchanger. Water is the working fluid used in the heat exchanger to allow heat recovery from the exhaust gases. This has also provided a condensing region for the water based oil. The HERU set-up is ultimately used to extract the energy content of the pyrolytic products for combustion, but for this paper pyrolytic products were extracted for analysis only.

As the temperature of the pyrolysis reaction is crucial to the products formed, K-type thermocouples were used to monitor the temperature in the reaction chamber. The thermocouples were placed on the legs of the heat pipes. The same experimental procedure and set-up used in this research is the same as that of Jouhara *et al.* [12].

3. Sample preparation

Samples for specific chemical elements content determination were dissolved in a heating block in a mixture of concentrated HNO_3 and 30% solution of H_2O_2 in quartz glass at 135 °C. The decomposition residues were diluted to 50 g. The samples, shown in Figure 3, were taken at different times as shown in Table 2.



Figure 3. Pyrolysis liquid and oily samples taken from the pyrolysis reactor.

Table 2. Time at which samples were taken from the process.

Sample	Time at which the sample was taken out from the pyrolyser from
	the beginning of the process
1	20 minutes
2	40 minutes
3	2 hours
4	4.5 hours
2', 3', 4'	Oily samples taken from liquid samples 2,3 and 4, respectively.

The oily samples in this paper are referred to as 2', 3', 4' or F2, F3, and F4, respectively.

4. Analytical techniques used for bio-oil analysis 4.1.FT-IR analysis

The Fourier transform–infrared spectroscopy (FT-IR) spectra of bio-oils were recorded on a **Vertex 70v** (Bruker GmbH) spectrophotometer. All samples were analysed in the wave number range of 4000–500 cm⁻¹. A photo of the FTIR equipment used for the analysis is shown in Figure 4.



Figure 4. A photo of FTIR analytical tool used for bio-oil analysis.

4.2.GC/MS analysis

The bio-oil was analysed by an HP6890 gas chromatograph equipped with an HP5973 mass selective detector and an HP-1701 capillary column (30 m x 0.25 mm x 0.25, 14%-cyanopropylphenyl-86%-dimethyl siloxane polymer). As a carrier, helium gas (purity 99.999%) was used. The column temperature was programmed from 40 to 260 °C at 10 °C/min after an initial 4 min isothermal period, and kept at the final temperature for 10 min. The inlet was set at 250 °C. Sample injection was made in the split mode (1:10). The mass spectrometer was set at an ionizing voltage of 70 eV with mass range m/z 15–400. The identification of organic compounds was accomplished by comparing mass spectra of the resolved components using electronic library search routines. A photo of the GC/MS used for the analysis is shown in Figure 5.



Figure 5. Photo of GC/MS analytical tool used for bio-oil analysis.

5. Results

5.1.FT-IR analysis

The FT-IR spectra of the bio-oils investigated are presented in Figure 6. These included bio-oil samples 2, 3 and 4. No bio-oil was extracted from sample 1 because the liquid content was essentially water.

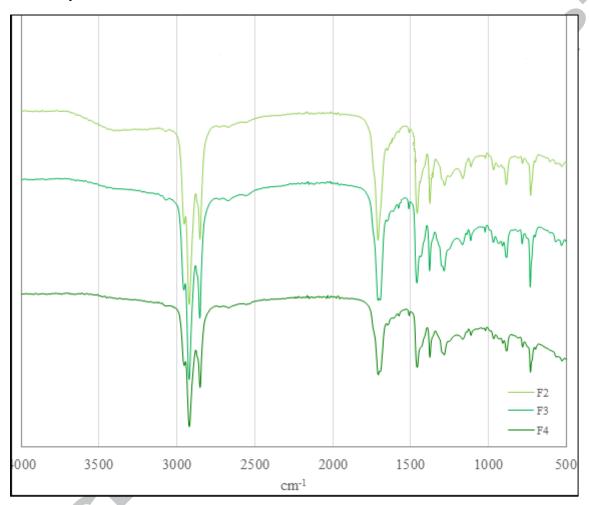


Figure 6. FTIR spectra of bio-oil samples 2, 3 and 4.

Bio-oil samples collected as fractions 2-4 are characterized by a high proportion of oxygen groups, represented on the FT-IR spectra as intensive adsorptions associated with the C=O stretching vibrations existing in the regions 1700-1720 cm⁻¹. These are accompanied by C-H bending vibrations with absorption location between 1370 and 1460 cm⁻¹, which can be attributed to the methyl and methylene groups. Alkane presence is confirmed by the IR absorptions in the region 2970-2850 cm⁻¹ (C-H stretching vibrations).

Adsorptions associated with the O–H stretching vibrations existing in the regions 3500–3200 cm⁻¹ are less intensive, indicating reduced amounts of compounds rich in hydroxyl groups.

5.2.GC/MS analysis

Results of GC/MS analyses are given in Table 2 and Figure 7 a-c. Moreover, selected ion chromatograms for bio-oil sample F3 have been selected for analysis because sample F3 is the bio-oil sample that consists of all bio-oil constituents of the previous samples. These selected ion chromatograms are shown in Figure 8 a-d.

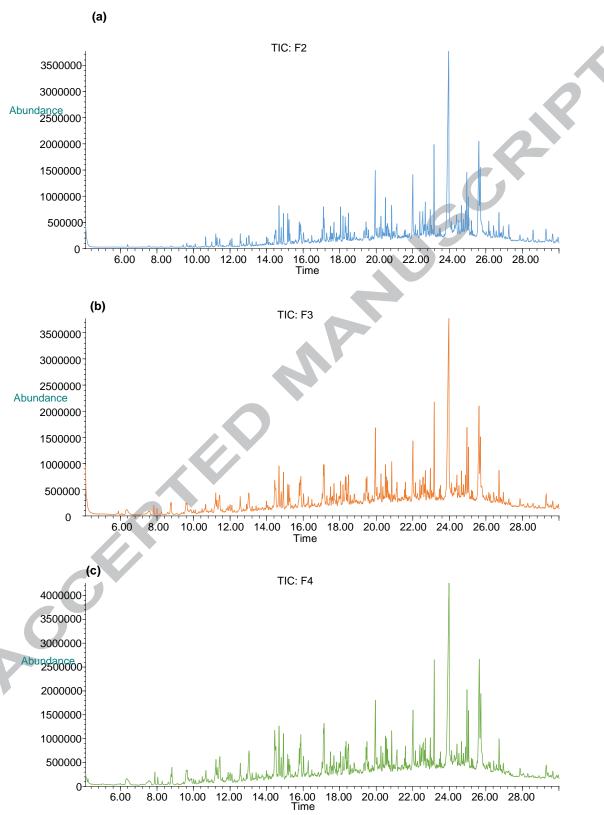


Figure 7a-c.Total ion current obtained during GC/MS analysis of bio-oil samples F2, F3 and F4, respectively.

Different groups of chemical compounds constitute the bio-oils produced from food by means of pyrolysis. Hydrocarbons, both saturated and unsaturated, and carboxylic acids (C12-C18) are the most abundant components of F2-oil, F3-oil and F4-oil. Small amounts of alkylbenzenes (including styrene and styrene dimer), phenanthrene and anthracene were also detected. Additionally, the presence of long-chain nitriles and amides is also noted in these fractions.

All bio-oils analysed contain carboxylic acids, which is visualised by characteristic ion chromatogram (m/z=60) in Figure 8a. According to the selected ion chromatograms, hydrocarbon chains below C6 were not present, whereas C8-C18 are present in F2-F4 oils. The most abundant are hexadecanoic acid, oleic acid and octadecanoic acid.

Figure 8b-c (characteristic ions m/z=55 and 57) clearly show that chain hydrocarbons are concentrated in oil fractions F2-F4. As it can be seen in Figure 8d, selected ion m/z=91 chromatograms, presenting the distribution of alkylbenzenes, confirm that hydrocarbons concentrate in samples F2-F4.

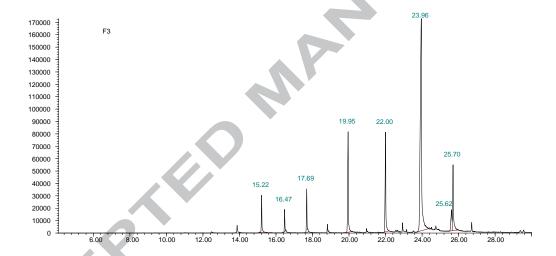


Figure 8a. Selected ion chromatograms (m/z=60 – characteristic for carboxylic acids) obtained during GC/MS analysis of bio-oil sample F3.

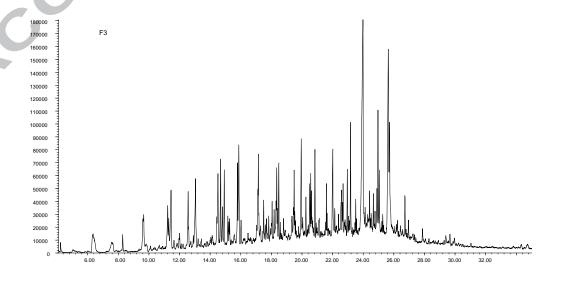


Figure 8b. Selected ion chromatograms (m/z=55 – characteristic for unsaturated hydrocarbons) obtained during GC/MS analysis of bio-oil sample F3.

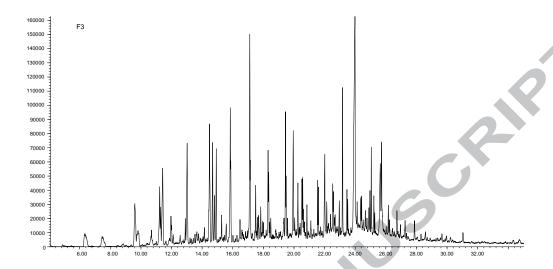


Figure 8c. Selected ion chromatograms (m/z=57 – characteristic for saturated hydrocarbons) obtained during GC/MS analysis of bio-oil sample F3.

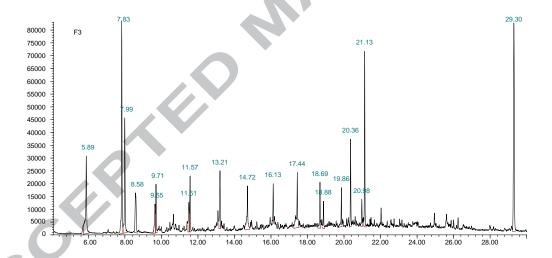


Figure 8d. Selected ion chromatograms (m/z=91 – characteristic for alkylbenzenes) obtained during GC/MS analysis of bio-oil sample F3.

Chemical compounds in the bio-oil samples were identified according to their retention time. The peak areas for each of the compounds indicate its relative presence and the compounds in red show the presence of a high amount of that particular compound in the corresponding bio oil sample. The results are shown in Table 3.

Table 3. Peak area (%) of selected compounds identified in F2, F3 and F4 bio-oils.

RT,		CAS	Peak area, %		
min	Compound	number	F2	F3	F4
6.395	2,4-Dimethyl-1-heptene	019549-87-2	0.65	0.678	0.711
7.829	Ethylbenzene	000100-41-4	0.274	0.262	0.278
8.578	Styrene	000100-42-5	0.264	0.266	0.205
9.633	1-Decene	000872-05-9	0.131	0.254	0.283
10.666	D-Limonene	005989-27-5	0.219	0.352	0.468
11.435	1-Undecene	000821-95-4	0.271	0.905	1.013
12.564	1-Undecene, 7-methyl	074630-42-5	0.23	0.639	0.721
12.905	Nonanal	000124-19-6	0.172	0.147	0.276
13.021	Dodecane	000112-40-3	1.218	1.124	1.602
13.043	1-Dodecene	000112-41-4	0.221	0.198	0.232
13.215	Benzene, pentyl-	000538-68-1	0.295	0.282	0.249
14.431	Naphthalene	000091-20-3	0.201	0.267	0.288
14.480	Tridecane	000629-50-5	2.256	2.058	1.658
14.509	1-Tridecene	002437-56-1	1.294	1.211	1.12
14.685	Cyclohexane, 1,1,3,5-tetramethyl-, trans-	050876-31-8	1.796	1.59	1.517
14.804	alkyl cyclohexane		0.433	0.655	0.729
14.925	alkyl cyclohexane		0.587	1.086	1.176
15.159	alkyl cyclohexane		0.584	0.727	0.702
15.225	alkyl cyclohexane		0.549	0.673	0.521
15.277	3-Decene, 2,2-dimethyl-	055499-02-0	0.211	0.288	0.347
15.839	Tetradecane	000629-59-4	1.352	1.325	1.391
15.870	1-Tetradecene	001120-36-1	1.522	1.545	1.758
16.025	Naphthalene, 2-methyl-	000091-57-6	0.476	0.56	0.778
16.128	Benzene, heptyl-	001078-71-3	0.235	0.265	0.288
16.284	Naphthalene, 1-methyl-	000091-57-6	0.274	0.424	0.881
16.473	Nonanoic acid	000112-05-0	0.218	0.139	0.246
17.111	Pentadecane	000629-62-9	1.658	1.159	1.18
17.147	1-Pentadecene	013360-61-7	1.722	1.146	1.273
17.445	Benzene, octyl-	002189-60-8	0.261	0.299	2.673
17.497	6-Tridecene, 7-methyl	024949-42-6	0.639	0.686	0.869
17.563	m/z 196		0.251	0.208	0.259
17.610	m/z 196		0.245	0.279	0.313
17.685	Decanoic acid	000334-48-5	0.865	0.91	0.987
17.829	m/z 196		0.284	0.313	0.378
17.959	Naphthalene, 2-ethenyl	000827-54-3	0.236	0.45	0.417
18.008	alkyl cyclohexane		0.187	0.268	0.277
18.051	alkyl cyclohexane		0.657	0.576	0.499
18.183	alkyl cyclohexane		0.668	0.616	0.639
18.306	Hexadecane	000544-76-3	0.996	0.954	0.945
18.345	1-Hexadecene	000629-73-2	0.634	0.619	0.656
18.398	Octadecanal	000638-66-4	0.28	0.294	0.326
18.685	Benzene, nonyl-	001081-77-2	0.229	0.347	0.452

19.341	8-Heptadecene	002579-04-6	0.699	0.723	0.702
19.441	Heptadecane	000629-78-7	0.565	0.805	0.77
19.483	1-Heptadecene	006765-39-5	0.331	0.633	0.91
19.859	Benzene, decyl-	000104-72-3	0.373	0.338	0.365
19.948	Dodecanoic acid	000143-07-7	2.188	2.691	2.333
20.258	m/z 238		0.888	1.036	0.876
20.359	Benzene, 1,1'-(1,3-propanediyl)bis-	001081-75-0	0.459	0.618	0.598
20.507	Octadecane	000593-45-3	1.038	1.186	1.036
20.566	1-Octadecene	000112-88-9	0.465	0.681	0.711
20.616	m/z 238		0.428	0.844	0.733
20.692	Oleyl Alcohol	000143-28-2	0.394	0.388	0.396
21.101	Benzene, ethenyl-, dimer	025247-68-1	0.197	1.136	1.048
21.543	Nonadecane	000629-92-5	2.776	2.997	2.605
21.590	1-Nonadecene	018435-45-5	0.702	0.827	0.733
22.003	Tetradecanoic acid	000544-63-8	0.817	0.828	0.582
22.469	Phenanthrene	000085-01-8	0.544	0.652	0.583
22.548	Anthracene	000120-12-7	0.965	0.888	0.755
22.63	Hexadecanoic acid, methyl ester	000112-39-0	0.569	0.549	0.513
23.029	Hexadecanenitrile		2.285	2.855	2.486
23.359	eicosane	000112-95-8	0.359	0.648	0.355
23.414	1-eicosene	003452-07-1	0.403	0.475	0.423
23.967	Hexadecanoic acid	000057-10-3	11.654	13.557	11.426
24.125	10-Octadecenoic acid, methyl ester	013038-45-4	0.737	0.831	1.162
24.396	Docosane	000629-97-0	0.974	0.949	0.721
24.886	Heptadecanenitrile		1.056	1.808	1.325
24.957	Tricosane		0.582	0.428	0.304
25.043	Octadecanenitrile		0.405	0.41	0.301
25.620	Oleic Acid	000112-80-1	4.585	4.965	4.673
25.700	Octadecanoic acid	000057-11-4	3.318	2.35	2.432
25.767	Tetracosane		0.698	0.621	0.265
26.790	Hexadecanamide	000629-54-9	0.852	0.447	0.255
27.260	Hexacosane		0.408	0.208	0.233
28.587	Heptacosane		0.597	0.653	0.481
29.290	Octacosane		0.358	0.329	0.239
29.571	Octadecanamide	000124-26-5			

5.3.Metal composition

Metal concentration in the liquid (water and oil), oil samples and ash are shown in Table 4-6. Calcium has a strong presence in comparison to the other metals, whilst potassium is present but at a low level. As one might expect, the oily samples have a greater concentration of the metals than the liquid samples.

Table 4. Concentration of metals in the liquid (1-4), oil samples (2'-4') and solid residue.

Sample	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
1	128.5±1.4	4.53±0.10	11.90±0.21	37.71±0.49
2	109.5±2.4	4.52±0.11	9.60±0.13	35.20±0.32
3	109.7±2.7	4.62 ± 0.04	10.04 ± 0.14	36.93±0.63
4	194.7±6.0	5.77±0.09	10.30±0.20	36.67±0.70
Ash	$(1.06\pm0.02)\times10^5$	$(4.86\pm0.16)\times10^4$	$(5.25\pm0.10)\times10^3$	$(4.88\pm0.02)\times10^4$
2'	482.2±12.1	3.14±0.06	40.92±0.86	60.56±0.85
3'	499.5±14.0	19.89±0.30	39.58±0.71	68.33±1.09
4'	$(1.03\pm0.03)\times10^3$	38.43±0.42	25.78±0.57	49.40±0.74

Heavy metals may occur in food residues, since the small amounts of them is essential for plants growth [28]. Moreover, traces of other waste materials can increase the amount of those elements in pyrolysis residues. The presence of cadmium and cobalt is almost negligible in both the watery and oily samples, whilst iron is present in larger concentrations relative to the other metals shown in Table 5.

Table 5. Concentration of metals in the liquid (1-4), oil (2'-4') samples and solid residue.

Sample	Al (mg/kg)	Cd	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Fe (mg/kg)
		(mg/kg)					
1	0.995±0.004	< 0.003	< 0.002	0.010±0.001	0.207±0.003	0.131±0.007	0.284±0.007
2	0.418 ± 0.005	< 0.003	< 0.002	0.005 ± 0.001	0.087 ± 0.003	0.090 ± 0.001	0.178 ± 0.003
3	0.239 ± 0.005	< 0.003	< 0.002	0.007 ± 0.001	0.076 ± 0.001	0.060 ± 0.004	0.204 ± 0.002
4	0.183 ± 0.005	< 0.002	< 0.002	0.007 ± 0.001	0.075 ± 0.001	0.040 ± 0.004	0.204 ± 0.004
Ash	$(2.20\pm0.02)\times10^4$	< 0.058	< 0.046	146±1	69.0±1.1	< 0.230	$(1.70\pm0.01)\times10^3$
2'	3.14±0.14	< 0.041	< 0.033	0.159±0.021	8.66±0.12	0.446±0.029	6.06±0.11
3'	2.53±0.04	< 0.026	< 0.021	0.396±0.039	3.99±0.10	0.414±0.028	9.27±0.03
4'	3.53±0.08	< 0.024	0.076±0.001	0.968±0.022	4.60±0.06	< 0.096	26.4±0.2

Sulphur is also present in high concentrations relative to the other elements shown in Table 6. The presence of Sulphur is related to the feedstock used in the reactor. Fruits and vegetables contain high concentrations of Sulphur which explains its occurrence in the liquid and ash samples. However, it must be taken into account that during thermal processing Sulphur contained in a feedstock may go through many reactions and create compounds - especially in evolved gases, that are potentially unsafe.

Table 6. Concentration of elements in the liquid (1-4), oil (2'-4') samples and solid residue.

Sample	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	S (mg/kg)	Sr (mg/kg)	Zn (mg/kg)
1	< 0.007	0.693±0.012	< 0.016	22.4±0.8	0.493±0.002	0.240±0.003
2	0.029 ± 0.002	1.30 ± 0.01	< 0.016	25.7±0.6	0.378 ± 0.004	0.164 ± 0.003
3	< 0.007	1.28 ± 0.02	< 0.015	22.1 ± 0.4	0.389 ± 0.006	0.108 ± 0.002
4	0.025 ± 0.002	1.34 ± 0.05	< 0.015	26.4 ± 0.3	0.412 ± 0.005	0.246 ± 0.002
Ash	100±1	$(9.46\pm0.02)\times10^3$	2.04 ± 0.14	$(5.85\pm0.09)\times10^3$	139±1	182±1

4	2'	< 0.11	2.57±0.14	< 0.25	241±2	3.70±0.03	2.01±0.01
3	3'	0.273±0.018	4.40±0.17	< 0.16	257±6	3.43±0.03	1.60 ± 0.01
4	4'	0.575±0.034	7.67±0.27	< 0.14	272±2	2.34±0.03	5.03±0.04

6. Discussion

As the main components of food are carbohydrates, fats, proteins, water, vitamins and several minerals, the results have reflected the presence of nitrogen-containing compounds such as nitriles and amides. However, the proportions and the exact composition depend on the food items. For example, bone is mainly composed of hydroxyapatite and collagen, water, proteins, fat and minerals such as calcium, phosphorus, sodium, potassium and sulphur. Whereas 80% of potato consists of water and the remainder carbohydrates, proteins, lipids, minerals and vitamins [12]. The presence of such minerals is clearly shown in the elemental analysis of the bio-oil samples. Metal concentrations of calcium and potassium increased with increasing pyrolysis time in the oil samples. However, the concentration of sodium and magnesium decreased with time. This is due to an unrepresentative sample being taken from the liquid samples. All of the liquid samples 1, 2, 3 and 4 clearly show an increase in the metal concentration with time until a plateau is reached. Therefore, the analysis of the initial liquid samples taken from the process are representative of the process products.

According to the chemical compounds observed in this experiment, a variety of straight chain alkanes, alkenes, and cyclo compounds have been observed. It is conclusive that the majority of the bio-oil compounds detected are long chains with various functional groups. Aromatic compounds have been detected but in very small amounts. This finding coincides with the study carried out by Jouhara *et al.* [29].

The composition of bio-oils clearly indicates the complexity of the raw materials used for the pyrolysis process. The differences observed in the composition of oil fractions show the significant influence of the temperature / time of the pyrolysis process on the composition. Generally, the decomposition products of the lignocellulosic part of the food are collected in the first stage of the process, whereas products of complex molecule decomposition evolve in later stages of the pyrolysis.

The use of heat pipe system in a pyrolysis reactor allows this experiment to be easily repeated and achieve similar results if the same procedure is followed and the same feedstock is used. However, the biggest influence on achieving similar product chemical characterisation repeatedly would be the feedstock itself, because food naturally decomposes in air. This changes the functional groups which in-turn would result in some minor changes of the pyrolytic products. The food used for this experiment is only few of many items used in households. However, it does represent a proportion of what food a typical household can be expected to be discard.

This research study has shown that the bio-oil products derived from the pyrolysis of food can be useful in that they contain chemical components that can be combusted to produce heat. The heat can then be used to heat up water. The other use of such good bio-oil components is that they could be blended with gasoline and diesel. This will enhance the

fuels' octane or cetane numbers, respectively, because of the significant amount of straight chain alkanes, alkenes, and cyclic compounds present in the bio-oil products.

7. Conclusion

This paper presents a novel heat pipe based pyrolysis unit and the chemical composition of food pyrolysis. The innovation of the system is that it provides efficient pyrolysis of the food at low temperatures (below 300°C) without the need of any kind of pre-treatment of the food prior to its loading into the apparatus.

The main components of the bio-oil are carboxylic acids and long chain hydrocarbons with various functional groups. The presence of nitrogen and carboxylic acid compounds were very strong throughout the experiment. The fluid obtained from the initial stages of pyrolysis, F1, had a similar composition to that of water, while the dense oil produced during the final stage of the process showed the formation of more complex compounds. The oil molecules obtained from the pyrolysis of discarded food are energy dense and could potentially provide a significant amount of heating value. The small presence of heavy metals in collected materials also indicates that throwing-away food is a good feedstock for pyrolysis.

Management of discarded materials is one of the most crucial challenges that developed countries are facing. The current treatment methods of discarded materials are inefficient in every aspect, whether it is environmental, economic and/or social. The HERU apparatus makes a positive contribution towards a circular economy and a sound environmental solution to the processing of such streams and at the same time it is a sustainable, and renewable, solution to energise our homes and business premises.

Moreover, the composition and properties of evolved gases from the pyrolysis must be done because emission limits from pyrolysis processes are very strict according to the European emission standards. Additionally, pyrolytic gases are usually a good source of gaseous fuel, and thus it could also be used for energy recovery.

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- Low temperature pyrolysis (lower than 300°C) of discarded food is reported
- Used Chemical testing methodologies are reported, and results are discussed.
- Resultants from the pyrolysis of the treated materials are detailed.

