Products' composition of food waste low-temperature slow pyrolysis

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Abstract. Food waste generation is one of the most crucial problems of our constantly developing world. There are several common methods of its treatment, however each one has its own advantages and disadvantages. Pyrolysis attracting attention in this field since a long time, because it allows to utilize this valuable resource with energy and material recovery. Moreover, the environmental impact of the process is relatively low. In this paper, products of low temperature household waste pyrolysis underwent a detailed chemical analysis. Liquid and solid residues was examined. Composition and concentration of particular compounds and elements indicates presence of long chain alkane, alkene and carboxylic acid molecules together with small amounts of aromatics within the bio-oil samples. The presence of heavy metals in residues was detected, too. Since the products are usually described as non-toxic, the idea of waste' low-temperature thermal treating in household was analyzed. In general, examined residues from the process are safe for the environment, thus pyrolysis can be considered as a legitimate mechanism to treat kitchen waste combined with energy recovery for homes.

1 Introduction

Waste food is 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 waste may be avoided (e.g. plate leftovers). The second group consists of plants and animals parts, which are not usually eaten (e.g. egg shells, peelings) [1,2]. The composition of typical food waste varies significantly depending on its origin. In general, animal products contain a lot of proteins and lipids; fruits, vegetables and grains are rich in carbohydrates. The elemental composition of basic nutrients indicates that significant amount of carbon is available, thus discarded food is easy to degrade [3]. It is worth noting, that pieces of packaging (plastics, paper, aluminium foil), paper tissues, toothpicks etc. also

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appear in waste from kitchen and impede biodegradation, but it does not contribute to any implications in the thermochemical decomposition.

Discarded food materials is a resource with enormous potential that became a more and more serious problem. As an example, in 2014 Food and Agriculture Organization estimated that annually food worth 936 billion USD was discarded around the world [4]. However, the cost of food wastage is much higher, since the indirect consequences of environment degradation should be included, too. Dumping food residues cause many serious problems. Environmental impact of this around the world is shown in Table 1. Unused food contributes to: GHG emissions; soil erosion and deforestation. Additionally, occupies almost million ha of land and causes enormous water consumption.

Table 1. Main global environmental impact of waste food [4].

Environmental impact	Unit	Global
GHG emissions	Gt CO_2e	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

What is more, many resources are wasted for transportation of unused food until it reaches its final destination. It is estimated that collection cost varies between 40 and 60% of all community's discarded materials management cost [5,6]. Additionally, energy intensive processes, such as sorting and grinding, are used for pre-treatment of food waste. Anaerobic digestion and composting have been successfully applied at household level. However, they need specific conditions and many times produce more problems than solving them, such as odours [7,8]. Additionally, the microorganisms are quite sensitive and carbon content in feedstock cannot be fully utilized, since it is partially accumulated in microbes [9,10]. Thus, there is an immediate need to find novel effective ways to cope with waste that are produced in households.

Kitchen waste is a rich source of energy. Therefore, it is a feedstock for thermochemical processes with great potential. Pyrolysis is the process of producing pyrolytic oil, syngas and biochar well-known since ancient times [5]. It is a process of thermal decomposition of any carbon-content feedstock that occurs in high temperature (between 300 and 1000°C) in the absence of oxygen. Usually it is conducted under atmospheric pressure; vacuum pyrolysis is less popular in practice, since it is generally more complicated [11]. It is possible to select the conditions of the process – especially temperature and residence time in the chamber – in order to obtain the most desirable products. Pyrolysis has been attracting an increased attention in resource-to-energy processes since a long time, because it has very important advantages. Firstly, pyrolysis allows the transformation of low-energy density discarded materials, into valuable bio-fuels [12,13]. Secondly, pyrolysis contributes to reduce corrosion and emissions by retaining majority of metals, sulfur and chlorine within the process residues. Formation of NO_X is also cut [5]. Finally, the scale of pyrolysis plant is more flexible than incineration plants. It is possible to use it even in a single household [14,15].

Pyrolysis of food waste for energy recovery and materials production has been applied in many previous studies, but the feedstock was in principle sorted, pre-treated (shredding, drying) and carefully chosen [16–18]. Food samples used in pyrolysis reactors in literature are: cereals [19]; peanut crisps [19]; potato peels [20]; soybean protein [21]; peelings and chopping's of various raw vegetables and fruits [22]; mixture of rice, vegetable and meat/bones [16], or even dog food [9]. An important advantage of this work is the fact that

discarded materials are not pre-treated in any special way and sample consist of real waste from kitchen in UK's household. Therefore, the composition of pyrolysis oils and solid residue is very realistic. Additionally, novel construction of chamber based on heat pipes [15] was used that allows the slow pyrolysis of waste food at 300°C with effective energy recovery through combustion of obtained biochar. Chemical analysis of pyrolysis oil and solid residue allows to check the safety and environmental impact of proposed solution.

2 Experimental

2.1 Pyrolysis

The experimental set-up consisted of a reaction chamber which was heated up and maintained at 300°C under control of electronic temperature unit. The feedstock was not prepared for pyrolysis in any special way. Drying and shredding were not necessary, since the uniform temperature at any location of the chamber is provided by heat pipes. Additionally, thermal insulation around the chamber prevented heat loss to the surrounding. The chamber was loaded with various mixtures of materials collected from the kitchen.

The liquid phase was collected once the feedstock is pyrolyzed and then condensed near 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 liquid. The device proposed by Jouhara *et al.* [15] is eventually used to extract the energy content of the biochar by combustion, but for this paper pyrolytic products were extracted for analysis only.

2.2 Samples preparation

From the process were taken 3 samples of products: early and late stage pyrolysis oil, and ash after combustion of biochar. First sample of oil was taken after 6 hours since the beginning of the process, second – after 8 hours. Earlier liquid samples was composed mainly of water, because of moisture evaporation from organic material. Samples are shown in Figure 1.
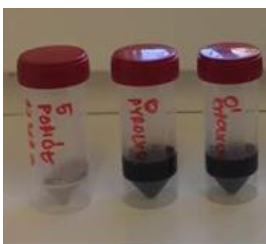
Fig. 1. Analysed samples from right to left: early stage oil, late stage oil and ash.

Before the analysis of metal content all samples was dissolved in a heating block in 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.

2.3 Analytical methods

Ash and oil samples were analysed for the content of heavy metals. Additionally, the presence and concentration of various organic compounds was checked in pyrolysis oils. Used analytical methods are described below.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is an analytical technique used for the detection of chemical elements. Produced excited atoms and ions emit electromagnetic radiation at wavelengths characteristic of a particular element, and the intensity of this emission shows the concentration of the element within the sample. In metal content analysis **Agilent ICP-OES 720** with axially-viewed plasma was used.

The Fourier transform–infrared spectroscopy (FT-IR) spectra of bio-oils were recorded on **Vertex 70v** (Bruker GmbH) spectrophotometer. Both oily samples were analysed in the wave number range of 4000–500 cm^{-1}.

The bio-oil was also analysed by an **HP6890 gas chromatograph** equipped with an **HP5973 mass selective detector** and a HP-1701 capillary column (30 m x 0.25 mm x 0.25, 14%-cyanopropylphenyl-86%-dimethyl siloxane polymer). Gas helium (purity 99.999%) was used as a carrier. The column temperature was programmed from 40 to 260°C at 10°C/min after 4 min isothermal initiation, 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). 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.

3 Results and discussion

3.1 ICP-OES analysis

The concentration of metals, which emissions from pyrolysis of waste are limited according to Industrial Emission Directive [23], in analysed liquid and solid samples are presented in Table 2. Heavy metals may occur in food waste, since the small amounts of them is essential for plants grow [24]. Moreover, traces of other waste materials can increase the amount of those elements in pyrolysis residues. Dong *et al.* [25] showed in their study that the proportion of heavy metals in the gaseous phase is increased gradually with temperature during thermochemical treatment of waste. Moreover, the type of atmosphere – redox or oxidative – poses great influences on the evaporation of heavy metals: cadmium (Cd) and zinc (Zn) are found to be more volatile under reductive atmosphere, whereas oxygen presence effectively promotes the volatilization of lead (Pb), copper (Cu), nickel (Ni), and chromium (Cr). Thus, it is important to check the concentration of heavy metals in residues from the analysed process, in order to ensure the safety of the proposed solution.

As it can be seen in the Table 2., the presence of cadmium is negligible in both solid and liquid samples. Lead appears in ash, but not in the oily samples, whereas mercury was detected in the liquid products. Chromium, copper, nickel and zinc were detected in all samples in higher amounts. As expected, the concentration of heavy metals was higher in ash than in oil. Additionally, late stage oil samples contained higher concentrations of metals than the samples that were collected earlier, except for copper.

Table 2. Concentration of metals (mg/kg) in samples from pyrolysis: 1.) early stage oil; 2.) late stage oil; and 3.) ash.

	Hg	**Cd**	**Pb**	**Cr**	**Cu**	**Ni**	**Zn**
1.	0.088±0.002	<0.005	<0.028	0.250±0.001	0.291±0.006	0.864±0.016	0.453±0.006
2.	0.246±0.015	<0.005	<0.029	0.593±0.008	0.228±0.003	1.34±0.04	0.464±0.007
3.	<0.230	<0.058	2.04±0.14	146±1	69.0±1.1	100±1	182±1

The concentrations of heavy metals in the analysed samples indicate that low-temperature, slow pyrolysis of food materials is an acceptable way to treat waste in households. However, the residues from the process should be treated in a controlled process, since the emissions limit values for discharges of waste water from the cleaning of waste gases in thermochemical waste treatment plants are very strict For example, mercury is limited to 0.03 mg/l; copper – 0.5 mg/l and zinc – 1.5 mg/l [23].

3.2 FT-IR analysis

The FT-IR spectra of tested pyrolysis oils are presented in Figure 2. Both oils, early and late stage, are characterized by broad and overlapping C–H stretching vibrations near 3000 cm^{-1}. Both bio-oils are rich in hydroxyl groups represented by signals in the range of wave number 3500–3200 cm^{-1}. This suggests the presence of high amounts of organic compounds rich in hydroxyl groups, glucose derivatives, organic acids and water.

Not only alkanes but also alkenes and aromatics are visualised on infrared spectra. The latter ones are represented by C=C stretching vibrations in the region between 1500 and 1680 cm^{-1}. The yields of aromatic compounds obtained through catalytic pyrolysis of food waste was an aim of the study conducted by Zhang *et al.* [26]. They detected relative content of total aromatics about 35% in 550°C.
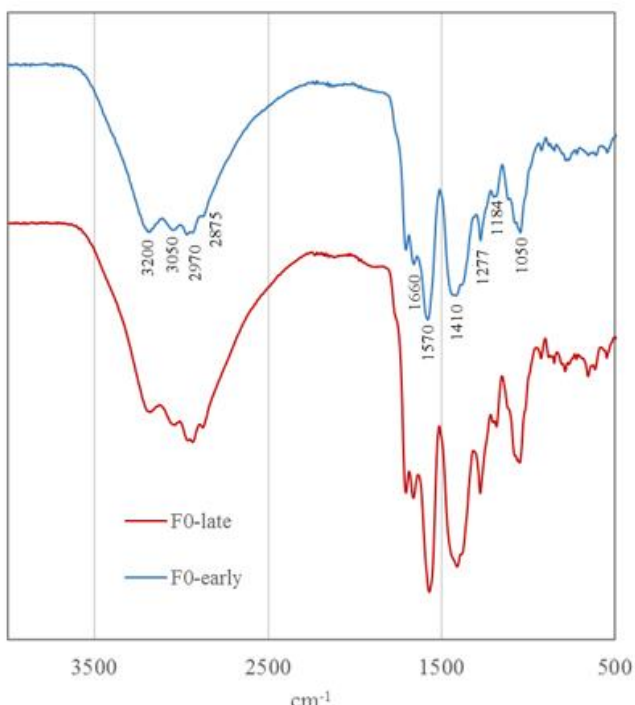

Fig. 2. FT-IR spectra of pyrolysis oils from kitchen waste.
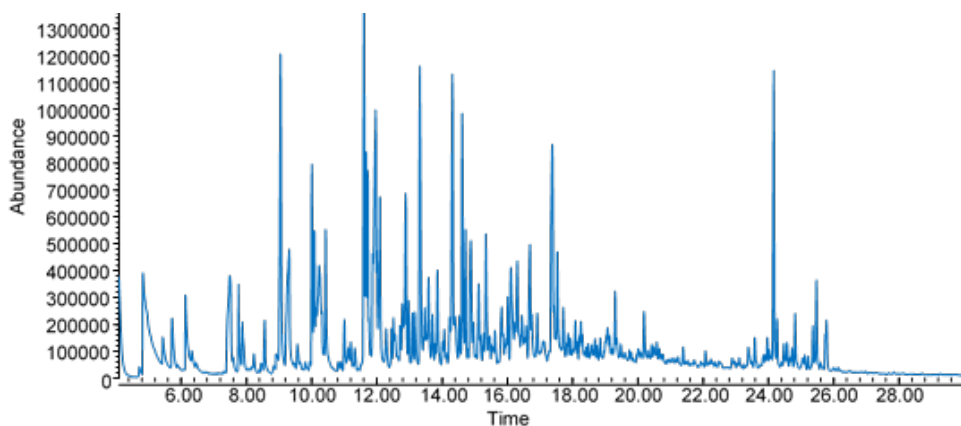
3.3 GS/MS analysis

Results of GC/MS analyses are given in Figure 3. and 4. Chemical compounds in the oil samples were identified according to their retention time (RT), and the peak areas for each of the compounds indicates its relative presence.

Different groups of chemical compounds constitute of bio-oils produced from mixed kitchen waste through pyrolysis. Bio-oils collected as early fraction and late fraction are mainly composed of hydroxyketones, phenols, carboxylic acids (C_2–C_8), pyridine and pyrazine derivatives, furan derivatives, butyrolactam, caprolactam and caffeine. Those results are comparable with previous studies carried out by Opatokun *et al.* [4]. They noticed significant amount of phenols, esters, ketones and acids in bio-oils from pyrolysis of food waste. The difference between early and late fraction is quantity of selected compounds, as can be seen on Figure 3. and Figure 4. 2-Furancarboxaldehyde, 5-methyl-2-furancarboxaldehyde and caprolactam are the most abundant components of early faction, with concentration 16.87, 9.8, and 5.67%, respectively. In the late fraction, there is no such dominance of any compounds, only concentration of acetic acid, 2-furancarboxaldehyde and butyrolactone exceed 3%.

Hydroxy ketones, for example 1-hydroxy-2-propanone and 3-hydroxy-2-butanone, were produced by degradation of sugars. Similarly, furan derivatives, e.g. 2-furancarboxaldehyde, 5-methyl-2-furancarboxaldehyde, 2(5H)-furanone which are dominant in early fraction, are the result of thermal conversion of cellulose or glucose. In addition, 1,4:3,6-dianhydro, alpha-glucopyranose is a result of thermal decomposition of carbohydrates, such as cellulose and starch. Alkylpyrazines are often formed during thermal processing of food.
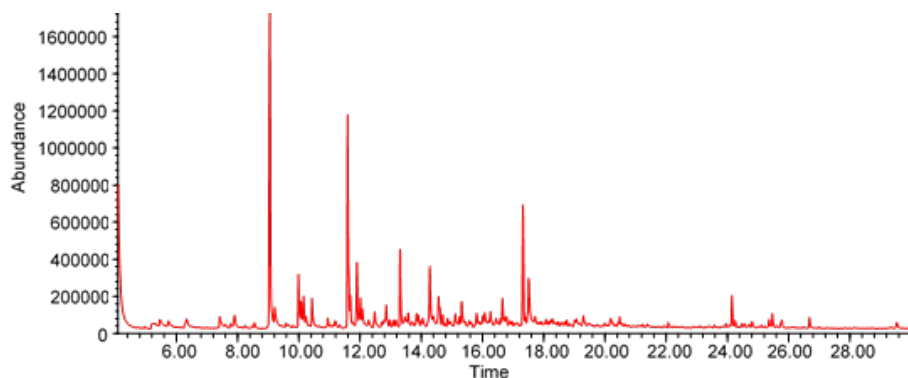
Fig. 3. Total ion current obtained during GS/MS analysis of early stage pyrolysis oil.

Fig. 4. Total ion current obtained during GS/MS analysis of late stage pyrolysis oil.

4 Conclusion and further work

This paper presents the chemical composition of residues from food low-temperature slow pyrolysis conducted in a novel heat pipe based apparatus. The major advantage of such process is that the waste does not require any pre-treatment prior to loading.

The composition of bio-oils clearly indicates the complexity of raw material used for pyrolysis process. The differences demonstrated in the composition of oil fractions show the significant influence pyrolysis process time on the composition. Generally, the products decomposition of lignocellulosic part of the waste were collected in the first stage of the process, whereas products containing more complex molecules evolved in later stage of the process. The presence of alkanes, alkenes and aromatics ware detected by FT-IR analysis. The collected pyrolysis oils were mainly composed of hydroxyketones, phenols, carboxylic acids, pyridine and pyrazine derivatives, furan derivatives, butyrolactam, caprolactam and caffeine. No harmful/toxic compounds were formed, which enforces the potential use of low temperature pyrolysis in the treatment of discarded organic materials. Moreover, the presence of only small amounts of heavy metals in both solid and liquid residues from the process is also promising. The possibility of household waste utilization through pyrolysis together with energy recovery seems to be an attractive option in comparison with traditional solutions.

In this study, liquid and solid residues derived from low-temperature, slow pyrolysis of household kitchen waste were examined. However, there is a concern about gaseous emissions from thermochemical processing of waste and they are limited in Industrial Emissions Directive [23]. Thus the next step of the research should be analysis of composition of exhaust gases from the pyrolysis.

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