Materials Science and Engineering, Volume 41, No.1. (2016) pp. 105-115.

THE EXAMINATION OF THE CO-PYROLYSIS OF FOOD AND WOOD I – SOLID RESIDUE

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Turning solid fuels into gaseous energy sources is getting more and more important nowadays. However, some amount of solid matter always remains after such processes. Based on the pyrolysis of base materials (food waste and oak) mixed in various mass ratios it can be determined that increasing the oak ratio leads to decreased fluid formation and increased gas yield. The high carbon content of the solid residue is also the result of the increased oak ratio of the base material mixture. Hence, its utilisation as fuel and base material for gasification is possible. The same conclusion can be drawn based on the high energy value of the solid residues. These two possible utilisations are enabled by the softening properties of both the base materials and the solid residues as well.

Keywords: co-pyrolysis, char

Introduction

Beside the utilisation of solid energy sources like fossil fuels, biomass or wastes via burning, the significance of gasification is becoming more and more important in energy production. This conversion requires a significant amount of energy but has many advantages: not only the energy utilisation of the gaseous energy sources is easier and applicable on a wider scale, but the gas produced via gasification can be base material for the chemical industry as well as fuel [1].

Torrefaction, pyrolysis and gasification are the main methods of thermochemical conversion. During torrefaction, the base material is heated up to 200–300 °C to remove the moisture and volatile content and to increase the energy density of the base material. Pyrolysis is usually performed between 400–600 °C in anaerobic conditions. As a result, a significant amount of liquid matter is formed and solid matter remains in the end of the process. During gasification, the base material is transformed into gaseous energy source at high temperature, around 1000–1500 °C. Some reactants used could be air, oxygen, steam or H_2 [2].

Depending on the technology used, some amount of liquid, gaseous or solid matter is formed during all three processes. The ratio of these materials depends on the base material and the technology chosen. In many cases, the carbon content of the residual solid matter (char) is rather high. Thus further gasification is possible, it may be used as fuel or as activated carbon in gas- and wastewater cleaning systems [3].

Food wastes are typically treated as municipal wastes and disposed in Hungary, while these are composted or utilised as base material for biogas production in countries with a long history of waste recovery [4, 5]. Such processes might require weeks or months based

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on the applied technology, while thermochemical processes require only hours. Thus, wastes can be converted to valuable resources in significantly less time.

Various food mixtures were pyrolised and the results revealed that these materials are appropriate for the production of good quality gaseous fuel. However, these wastes have high moisture content, typically at least 40 wt%, and are not generated in such high content, so their production is not economic. To solve this issue, supplementary base material was added to the mixtures for further experiments [6].

Based on our previous examinations, [7] woody biomasses might be the most appropriate for co-pyrolysis and the most optimal temperature should be 700 °C for pyrolysis. Our various base material mixtures were also pyrolised on 700 °C and the produced gases, fluids and solid residues were analysed. The current article consists of the analysis of only the residual pyrolysis char from the reactor.

1. Base materials and the examination method

The base material for the pyrolysis experiments was food waste and oak mixed in various mass ratios. The composition of food waste was always the same: cooked rice (25 wt%), French fries (25 wt%), fried chicken breast (25 wt%) and breaded pork chop (25 wt%). The names of the samples and their meanings are in Table 1.

Table 1
The names of the samples in the article

Name of the sample	Note
Food	Original food mixture of cooked rice (25 wt%), French fries (25 wt%), fried chicken breast (25 wt%) and breaded pork chop (25 wt%)
2 Food:1 Wood	2:1 mixture of food mixture and oak mixture
1 Food:2 Wood	1:2 mixture of food mixture and oak
Wood	Original oak
Food – 700°C	Pyrolysis char of food mixture (700 °C)
2 Food:1 Wood – 700 °C	Pyrolysis char of 2:1 mixture of food mixture and oak (700 °C)
1 Food:2 Wood – 700 °C	Pyrolysis char of 1:2 mass ratio food mixture and oak (700 °C)
Wood – 700 °C	Pyrolysis char of oak (700 °C)

An experimental reactor has been built (Figure 1) in which the pyrolysis experiments were carried out until the gas production was detectable.

The examination methods for the base materials and pyrolysis chars were the following:

Standard “*EN 14775:2010: Solid Biofuels – Determination of Ash Content*” was used to determine the ash content. The analysis was carried out in a HK-45/12 V type heating furnace with 12 kW nominal power.

The elemental composition of the samples was analysed based on Standard “*EN 15104-2011: Solid Biofuels – Determination of Total Content of Carbon, Hydrogen and Nitrogen – Instrumental Methods*” with a Carlo Erba EA 1108 elemental analyser. Program Eager 200 was used to collect and analyse the data.

Standard “*EN 14918:2009: Solid biofuels – Determination of calorific value*” was the basis of the determination of higher heating value (HHV), using a Parr 6200 type calorimeter, then in the light of certain corrections, i.e. the hydrogen or moisture content of the sample, the lower heating value (LHV) was calculated.

The softening and melting properties of the ash ware analysed with a SYLAB IF2000G type instrument a based on Standard *“CEN/TS 15370-1: 2006: Solid biofuels – Method for the determination of ash melting behaviour. Characteristic temperatures method”:*

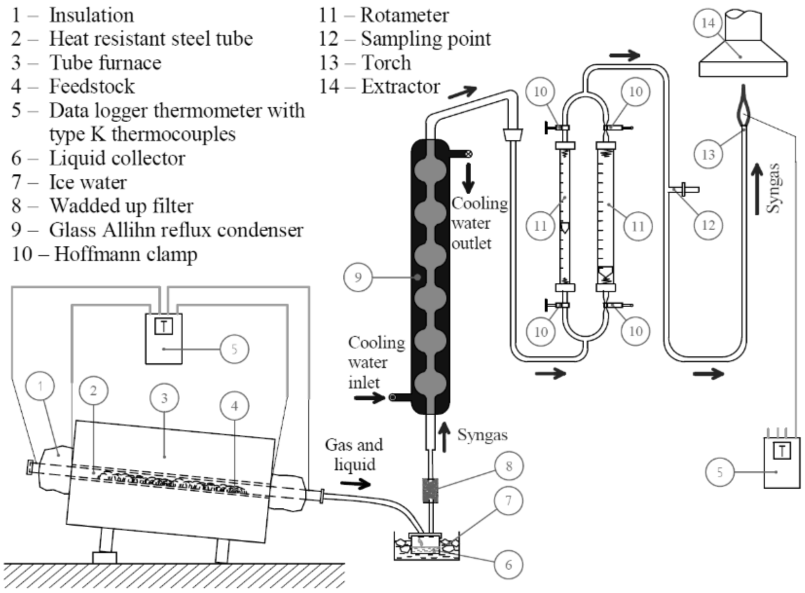

Figure 1
Schematic illustration of the experimental reactor

2. Results

2.1. Conversion of the base material

The different base materials leave the reactor partly in liquid and in gaseous form during the pyrolysis, but the ratio of the mass flows may change. Table 2 contains information on the quantity of the produced gaseous and liquid products and the remaining solid matter, while the conversion of the base material depending on the ratio of food waste and oak is illustrated in Figure 2.

Analysing the ratio of the produced materials in relation to the base materials (Figure 2) it can be determined that the wood added to the food mixture increased the gas yield and the quantity of residue char, and significantly decreased the amount of liquid produced. These values can be estimated via the first- and second-degree equations indicated in Figure 2.

Table 2
The mass ratio of the materials produced during pyrolysis (T = 700 °C)

Materials produced	**Mass ratio of the materials produced from various base materials, wt%**			
	Food	2 Food:1 Wood	1 Food: 2 Wood	Wood
Pyrolysis char	13.20	25.40	30.20	34.10
Liquid	64.01	49.95	41.96	36.42
Gas	22.79	24.65	27.84	29.48

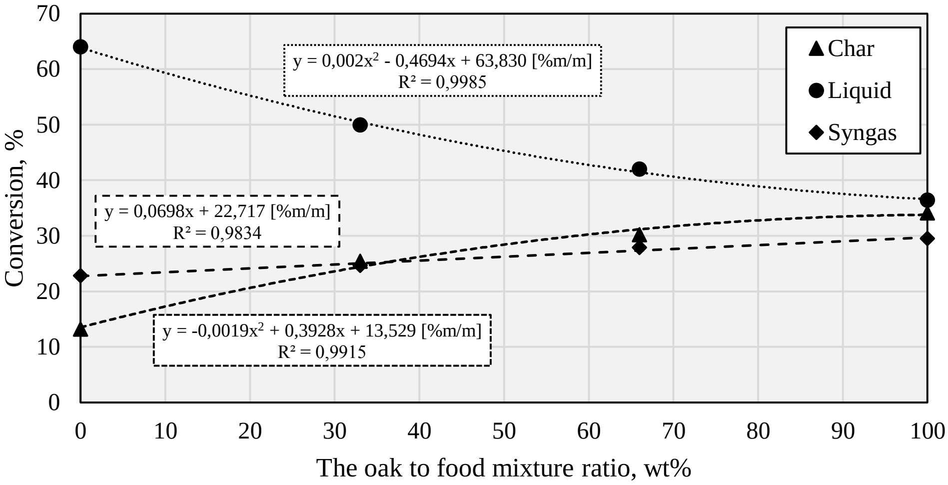

Figure 2
The ratio of the materials produced during pyrolysis (T = 700 °C) depending on the composition of the base material

2.2. *The composition of the base materials and the solid residues*

The comparison of the base and residue materials indicates that the carbon content of the solid residue is relatively high (Table 3). This property enables the further energetic utilisation of residues, like gasification or combustion. Furthermore, the structure of the solid residue was loose and porous (Figure 3) with high carbon and oxygen and low ash content. Therefore, these residues are suited for activated carbon production [8].

Further information can be obtained by comparing the elemental compositions of the residue char from 1 kg pyrolised base material and 1 kg base material. The carbon and oxygen contents of these are presented in Figure 4 and the nitrogen, sulphur and hydrogen content in Figure 5.

Table 3
The composition of the base materials and the remaining pyrolysis chars

Sample	**Average composition of the dry samples, wt%**					
	Nitrogen	**Carbon**	**Hydrogen**	**Sulphur**	**Oxygen**	**Ash**
Food	5.07	45.84	7.89	2.17	35.90	3.13
2 Food:1 Wood	3.22	45.98	7.33	1.45	36.98	5.04
1 Food:2 Wood	1.72	47.11	6.71	0.80	38.67	4.99
Wood	0.11	47.79	6.19	0.01	39.98	5.92
Food – 700 °C	4.61	62.92	3.51	0.45	16.45	12.06
2 Food:1 Wood – 700 °C	1.53	80.24	1.28	0.39	10.58	5.98
1 Food:2 Wood – 700 °C	0.77	79.85	2.59	0.30	10.23	6.26
Wood – 700 °C	0.17	83.49	2.43	0.32	11.99	1.60

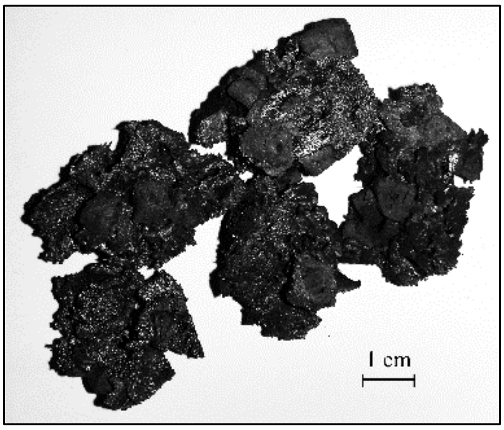

Figure 3
Photo of the char (2 Food:1 Wood – 700 °C)

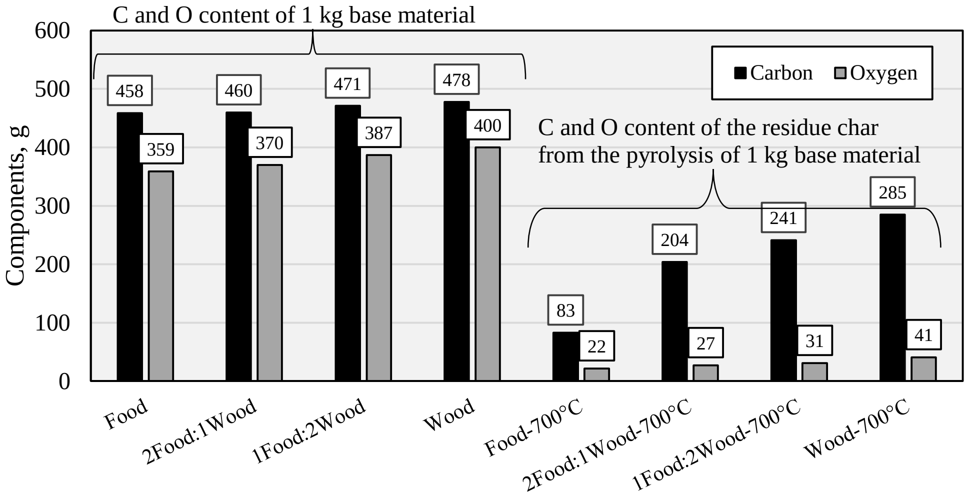

Figure 4
Carbon and oxygen content of 1 kg base material and its residue char (T = 700 °C)

The carbon and oxygen content of all four base materials are approximately the same, but the residue carbon increases in proportion to the amount of oak in the samples. This is in close relation to the facts that the carbon content of the residue char increases in proportion to the amount of oak in the base material. Moreover, the amount of the residue solid matter also increases with the amount of oak in the samples, as seen in Figure 2. The same can be stated in case of the oxygen in the residues, though, the increase ratio is not as high as in case of carbon.

The nitrogen, sulphur and hydrogen content of 1 kg base material decrease in proportion to the oak content of the base material but only a small proportion of these elements can be found in the char after pyrolysis. The low sulphur content of base materials is favourable during energy utilization.

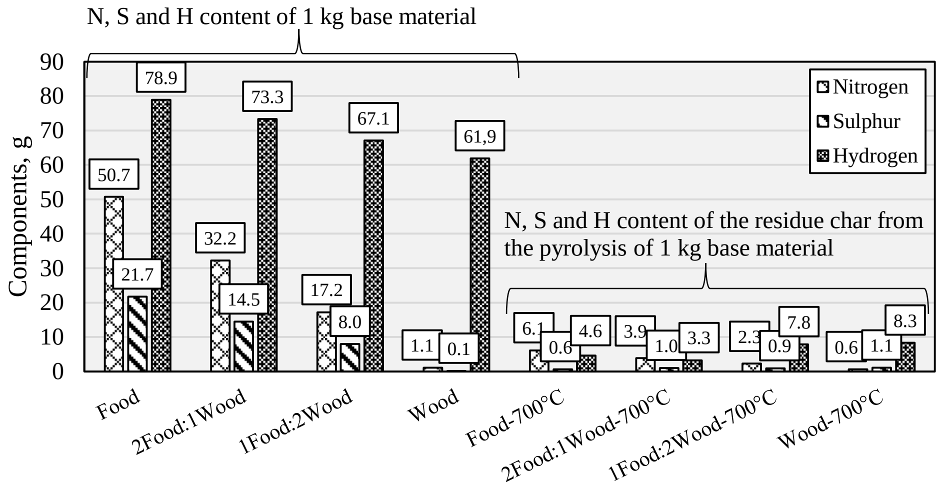

Figure 5

Nitrogen, sulphur and hydrogen content of 1 kg base material and its residue char (T = 700 °C)

2.3. Examination of the LHV

Based on the Figure 6 it can be stated that the LHVs of the char samples where higher than the LHVs of the base materials. The explanation is that the char contains relatively high amount of carbon, while the concentration of other elements is significantly low. Thus, as the carbon content is higher in the char than in the base materials, the LHV increases. Moreover, the increasing oak content of the base materials enhances the LHV as well. As the previous chapter proved, the quantity of the residue char from 1 kg base material also increases in proportion with the amount of wood. Based on these data, the heat value of the char is improved by the addition of oak.

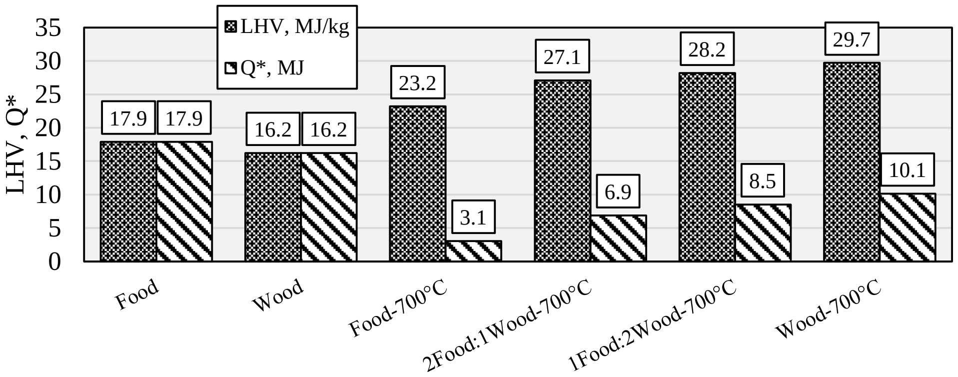

Figure 6

The LHV values and the released heat of the base materials and the residue char samples

(Q – The amount of released heat in case of the burning of 1 kg original base materials, and the amount of released heat in case of the burning of the residue char from 1 kg base material samples)*

The charting of the LHV and the energy value of the chars in relation to the composition of the base materials (Figure 7) shows that the estimation can be approximated with a second-degree equation. Thus, the estimation of the LHV of the residue char from various base materials is possible.

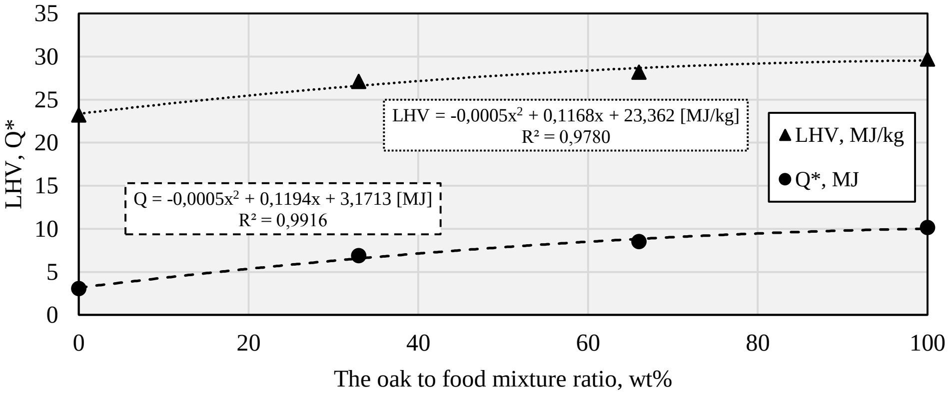

Figure 7
The LHV and the energy of the chars in relation to the composition of the base materials after pyrolysis (T = 700 °C)

Even though the LHV is more relevant in practice, data and literature on the higher heating value is more widespread [9, 10]. The HHV of the samples can be compared to various fuels in Figure 8. As the data in the various literature can be rather different, the average of these values can be found in the diagram without the exact value given. As the diagram clearly shows, the char samples are suitable for burning because the HHVs were higher than some of the already used fuels. Thus indicating the exact values was not necessary.

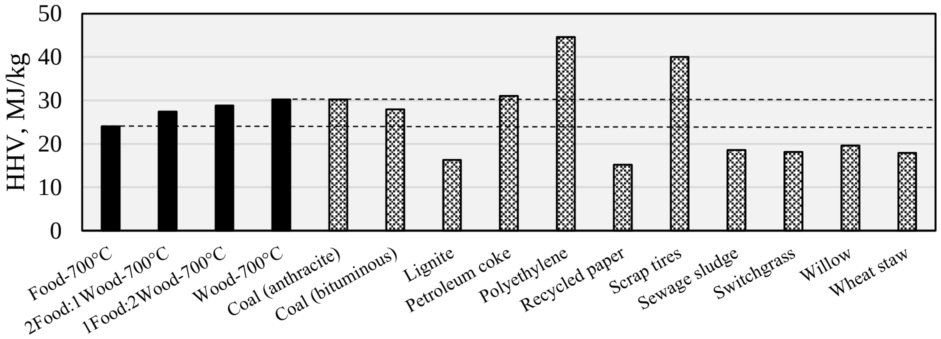

Figure 8
The char samples and some other materials used for energy recovery

2.4. The examination of the softening properties of the base materials and solid residues

The examination of the ash content revealed that the ash of the base materials has a much lighter colour than the ash of the pyrolised char samples (Figure 9) which implies that some kind of transformation takes place in the ash during pyrolysis. If these processes deteriorate the softening properties of the ash, the utilisation of the char at high temperature might become difficult.

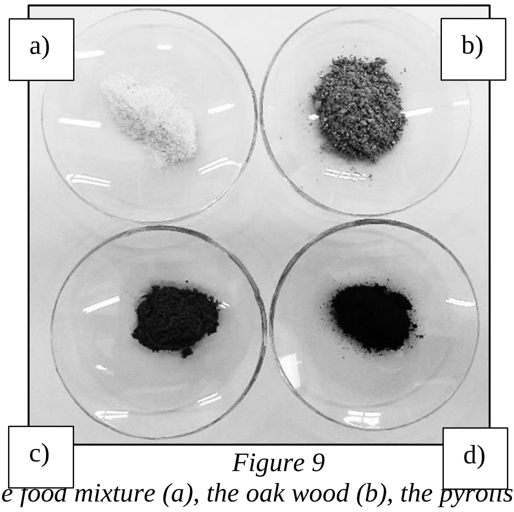

Figure 9
The ashes of the food mixture (a), the oak wood (b), the pyrolised food mixture (c) and the pyrolised oak (d)

In order to find out if any other properties of the ash change beside the colour, the softening parameters were examined. The deformation of the test bars prepared from the ash, based on standard *CEN/TS 15370-1: 2006,* because of temperature increase can be characterised with the following 5 states/temperatures (Figure 10):

1 – Original sample;

2 – Shrinkage starting temperature: the area of the test bar decreases by 5% because of sintering, the departure of CO_2 and/or volatile alkaline metals;

3 – Deformation temperature: the temperature at which the softening of the test bar seems to start, i.e. the surface is changing, the edges are getting rounded, the test bar is starting to swell. The starting temperature of the softening;

4 – Hemisphere temperature: the temperature at which the shape of the test bar resembles a hemisphere. The height of the molten test bar is the half of its diameter;

5 – Flow temperature: the temperature at which the height of the test bar is the half of the height measured at hemisphere temperature.

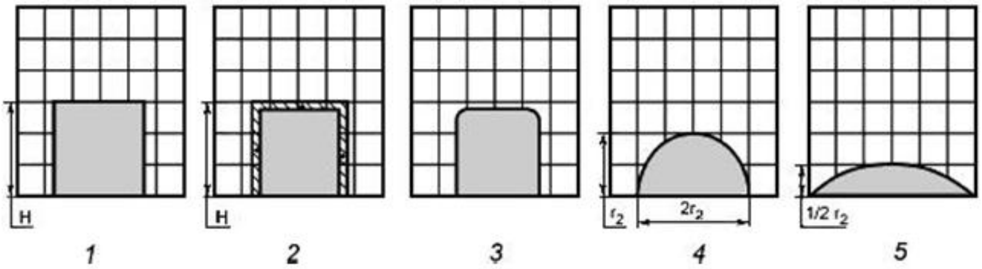

Figure 10
Phases in the ash melting process [11]
1 – Original sample; 2 – Shrinkage; 3 – Deformation; 4 – Hemisphere; 5 – Flow

Figure 11 illustrates the deformations of the test bars made out of the ashes of the original base materials and char samples, while Table 4 and 5 show the characteristic temperatures that can be found in the standard.

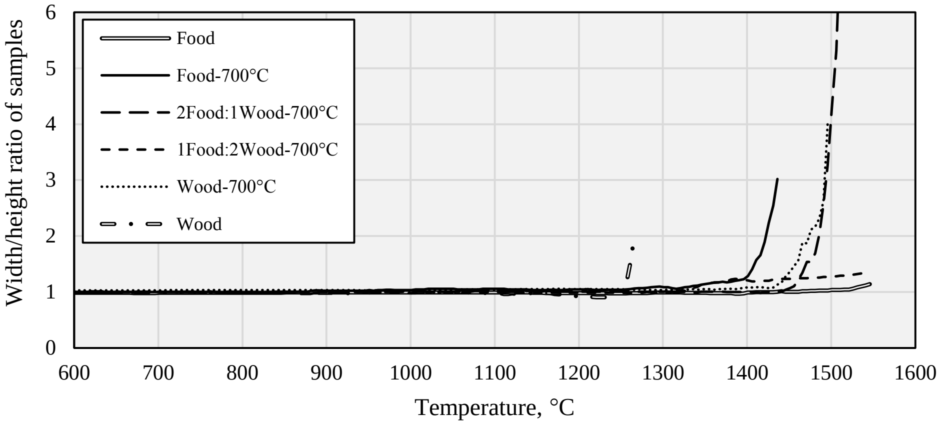

Figure 11
The width/height ratio of the ash test bars in relation to the temperature

The analysis of the width/height ration of the test bars showed (Figure 11) that the softening of the ash of the Wood sample had the lowest and the ash of the Food sample had the highest softening temperature. The softening properties of all the other residue samples were between these two temperatures.

Table 4
The properties of the ash of the original and pyrolised food mixture and oak

Properties	**Food**	**Food – 700 °C**	**Difference from the original**	**Wood**	**Wood –700 °C**	**Difference from the original**
Shrinkage starting temperature, °C	1396	1321	–75	1221	1192	–71
Deformation temperature, °C	1420	1263	–157	1076	1264	+188
Hemisphere temperature, °C	>1546	1423	>–123	1270	1472	+202
Flow temperature, °C	>1546	>1436	–	>1276	>1496	–

The comparison of the data from Table 4 reveals that the starting temperature of the sintering of the ash decreased a bit because of the pyrolysis. The deformation of the ash from the pyrolised food mixture started 157 °C lower than the deformation of the ash of the food mixture. On the other hand, the deformation of the ash of the oak started at a lower temperature in case of the original ash, not the pyrolised sample. This can also be observed at the hemisphere temperature. The flow temperature was too high to determine with our current equipment in all cases.

According to the analysis of the ash of the pyrolised materials (Table 5), sample “*1 Food:2 Wood – 700 °C*” was the first material to sinter, at 1071 °C, and to soften as well, at 1253 °C, latter of which temperature is too high to utilise the char by burning or gasification without causing problems in the system with the ash softening.

Table 5

The softening properties of the ashes of the pyrolised materials

Properties	**Food – 700 °C**	**2 Food: 1Wood – 700 °C**	**1 Food: 2 Wood – 700 °C**	**Wood – 700 °C**
Shrinkage starting temperature, °C	1321	1341	1071	1192
Deformation temperature, °C	1263	1450	1253	1264
Hemisphere temperature, °C	1423	1485	1526	1472
Flow temperature, °C	>1436	1508	>1546	>1496

The charting of the data from Table 5 can be observed in Figure 12.

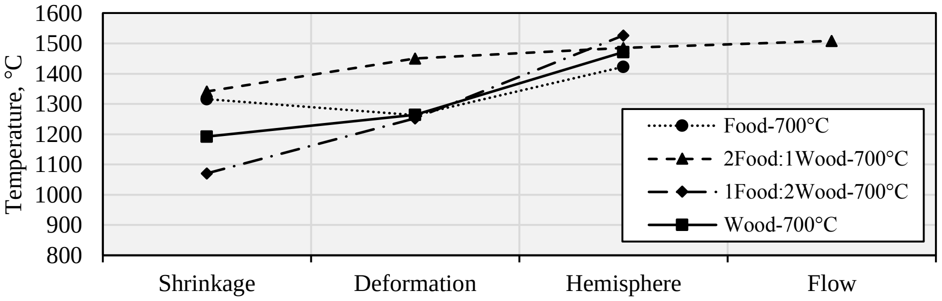

Figure 12

The softening temperature of the ashes of the pyrolised mixtures

Conclusions

The examination of oak and food waste mixtures in various mass ratios before and after pyrolysis at 700 °C shows that the conversion ratio of the base material decreases with the addition of oak, as the amount of solid residue is higher. Decreasing the ratio of oak resulted in less liquid and more gas production. The quantity of solid, liquid and gaseous products can be estimated based on the ratio of the base materials using first- and second degree equations.

The carbon content of the residue solid matter is relatively high after pyrolysis and increases with the higher ratio of the oak added to the base material. Furthermore, the char can be utilised not only as base material for gasification or energy recovery because of the high oxygen, low ash and sulphur content, but for activated carbon production as well.

The possibility of the usage for energy recovery was supported by the results of the LHV tests. A function was developed to estimate the LHV of the residue material of the pyrolysis of the mixture and another to determine the energy of the char from the pyrolysis of 1 kg base material, depending on the food mixture/oak mass ratio.

The examination of the softening properties of the ash of the original materials and pyrolysis chars showed that most of the characteristic temperatures are decreased by pyrolysis. Still, these temperatures are within such temperature range, that the softening of the ash should not cause any problems during neither gasification, nor burning.

Acknowledgement

This research was carried out in the framework of the Center of Excellence of Sustainable Resource Management at the University of Miskolc.

This research was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁMOP-4.2.4.A/ 2-11/1-2012-0001 'National Excellence Program'.

The authors are grateful to Mária Ambrus for her advice.

References

[1] BASU, P.: *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory.* Second Edition. Elsevier Inc., Burlington, 2013.

[2] BATHOLY, J.–BREUER, H.–PIECZKA, I.–PONGRÁCZ R.–RADICS K.: *Megújuló energiaforrások.* 2013.

[3] REZAIYAN, J.–CHEREMISINOFF, N. P.: *Gasification Technologies: A Primer for Engineers and Scientists.* CRC Press, 2005.

[4] ROSENWINKEL, K-H.–KROISS, H.–DICHTL, N.–SEYFRIED, C-F.–WEILAND, P: *Anaerobtechnik. Abwasser-, Schlamm- und Reststoffbehandlung, Biogasgewinnung. 3. Auflage*. Springer Verlag, Berlin–Heidelberg, 2015.

[5] MONIER, V.–MUDGAL, S.–ESCALON, V.–O'CONNOR, C.–GIBON, T.–ANDERSON, G.–MONTOUX, H.–REISINGER, H.–DOLLEY, P.–OGILVIE, S.–MORTON, G: *Preparatory study on food waste across EU 27.* Technical Report. European Commission, 2011.

[6] NAGY G.–WOPERÁNÉ SERÉDI Á.: Élelmiszerhulladékok energetikai hasznosítása. *Magyar Energetika,* 2014. 4. szám, 36–39.

[7] NAGY G.–KOÓS T.–WOPERÁNÉ SERÉDI Á.–SZEMMELVEISZ T.: Ételmaradékok kigázosításához kiegészítő alapanyag választása termoanalitikai vizsgálatok alapján. *Anyagvizsgálók Lapja*, 2014, 1–2. szám, 33–40.

[8] LÁSZLÓ, K.–BOTA, A.–NAGY, L. G.: Comparative adsorption study on carbons from polymer precursors. *Carbon*, Vol. 38, No. 14 (2000), 1965–1976.

[9] LACKNER, M.–WINTER, F.–AGARWAL, A. K.: *Handbook of Combustion*. Wiley–VCH, 2010.

[10] DEMIREL, Y.: *Energy – Production, Conversion, Storage, Conservation, and Coupling*. Springer, 2012.

[11] *CEN/TS 15370-1: Solid biofuels. Method for the determination of ash melting behaviour. Characteristic temperatures method.* 2006.