LABORATORY PYROLYSIS AND COMBUSTION OF POORLY TREATABLE BIOWASTES

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Pyrolysis of two types of biowaste whose use and processing are problematic, orange peel and apricot stones, provided a gas with a lower heating value of 11–14 MJ/m³, which can be, after improving, further used as the energetic gas. The obtained bio-oils exhibited a higher heating value of 30–32 MJ/kg and may be used as fuel oils; considering the large number of organic substances present in these oils, they can be alternatively utilized as a source of chemicals. Moreover, the pyrolysis further produced 27–29 wt.% of solid carbonaceous residue with a higher heating value of 33–35 MJ/kg, so, it may be used as auxiliary fuel for common solid fuels. Considered biowastes were further combusted and utilization of ashes obtained was investigated. It was found that ashes from the types of wastes studied can be used for the preparation of fertilisers for agricultural lands, because they contain significant amounts of essential elements – phosphorus, potassium and magnesium as well as calcium and sulphur.

1. Introduction

The results available have shown that pyrolysis is a very suitable process of effective treatment of biowaste and an alternative for combustion processes [1,2]. Using pyrolysis, it is possible to convert the types of biomass, whose treatment is otherwise difficult, into valuable products – an energetic gas heating oils, chemicals and sorbents. The most frequently pyrolysed biowastes are wood biomass and straw [3,4,5], the co-pyrolysis of rapeseed cake with coal was also studied [6]. It is indisputable that the most valuable pyrolysis product is oil, which has a wide range of applications – in heat, electricity and fuel productions as well as in the chemical industry. The amount of this product depends mainly on the character of incoming biowaste, further on the lignin to polysaccharide ratio [2], and on the process conditions (heating rate, a final temperature, a grain size, and a scale of pyrolysis). Slow conventional pyrolysis at a 5–10 °C/min yields ca 30% of liquid share, ~35% of gas and ~35% of solid pyrolysis residue, whereas fast pyrolysis (e.g. at 1000 °C/s) produces ~75% of liquid share, ~13% of gas and ~12% of solid residue [7]. In comparison with fast pyrolysis, however, conventional pyrolysis is technically more feasible and does not require a complex pre-treatment of the material being pyrolysed. Principally, any type of biowaste may be pyrolysed, but the utility properties of the products obtained and their yields depend, as mentioned, on the character of the biowaste and the process conditions.

In the given case, two types of problematic biowaste were selected for thermal decomposition by conventional pyrolysis. The first was orange peel, a waste product of the treatment of citrus fruits. During composting, it rots and produces pathogens, which are released into the soil; therefore, it should not be used in this way. A suitable combustion technology has not been developed yet. The second biowaste selected were apricot stones, a by-product of apricots processing, which are also difficult to compost; also in this case, the combustion technology has not been developed. Pyrolysis thus seems to be a suitable method for the treatment of both of these wastes.

If we consider combustion, the only product for further use is ash. Ashes from wood are possible to be used as fertiliser, either directly or after modification, because they often contain a distinct share of potassium and calcium (e.g. 10–30 wt.% K₂O and 17–56 wt.% CaO [8,9]). These ashes are entirely realistically considered as the base of soil-friendly fertilisers [10].

The aim of this work is therefore (a) to demonstrate the suitability of the pyrolysis method for the thermal treatment of both problematic types of biowaste, (b) to describe the utility properties of the products obtained and their yields, and (c) to describe the composition of ashes from laboratory combustion and outline their potential use. Wood biomass, namely birch wood sawdust, has been selected for a comparison.

2. Experimental part

2.1. Pyrolysed materials

Prior to the actual experiment, the samples were first air-dried (~20 °C, to the const. weight) and subsequently ground to a grain size of less than 3 mm; in the case of apricot stones, before the air drying they were roughly crushed with a jaw crusher. Birch sawdust samples were obtained by grinding of pre-dried shavings.

The pyrolysed biowaste samples weighed 100 g, birch sawdust samples 70 g. The charge of the birch sawdust was smaller because of its relatively lower bulk density 147 g/dm³ (the bulk density of the dry ground orange peel was of 278 g/dm³ and that of the dry ground apricot stones 583 g/dm³). The proximate and ultimate analyses of the pyrolysed samples are shown in Table 1.

Table 1 Proximate and ultimate analyses of the two biowastes and a comparative biomass (birch sawdust). BS – birch sawdust, OP – orange peel, AS – apricot stones

	Proximate analysis (wt.%)			Ultimate analysis (wt.%)					HHV (MJ/kg)
	W	A	VM	C	H	N	S_o	O_{dif}	
BS	6.51	4.62	81.66	52.30	6.34	0.62	0.04	40.70	21.02
OP	9.67	2.26	81.33	45.50	6.28	0.70	0.03	47.49	18.22
AS	4.87	2.42	87.83	60.41	8.38	7.14	0.18	23.88	26.96

W – water, A – ash (dry basis), VM – volatile matter (dry ash free basis), HHV – higher heating value.

It arises from Table 1 that the pyrolysed samples had a low ash and high volatiles contents, contained different amounts of carbon, oxygen and nitrogen and had quite different higher heating values.

2.2. Methods

Samples of biowaste and comparative woody biomass were pyrolysed in a laboratory unit with a fixed bed of our own construction. This unit has a vertical quartz reactor placed in an electric resistance furnace while the samples are heated at a rate of 10 °C/min to a final temperature of 600 °C with a thirty-minute dwell at this temperature; all the products formed are captured. The gases released are continuously analysed by an infrared analyser (Teledyne Analytical Instruments, Model 7500), the total gas is chromatographically characterised ([11], see below).

During the heating, volatile products were gradually released; initially, the temperature of the outgoing gas was 250–300 °C. The raw gas was cooled by two coolers with a circulating ethanol with temperature of about -10 °C. The condensing volatiles were collected in a flask and formed a liquid phase with bio-oil; the cooled gas rid of volatiles was collected in a gas holder as pyrolysis gas. For both types of biowaste and the comparative birch sawdust, the development of the gas produced is illustrated in Fig. 1.
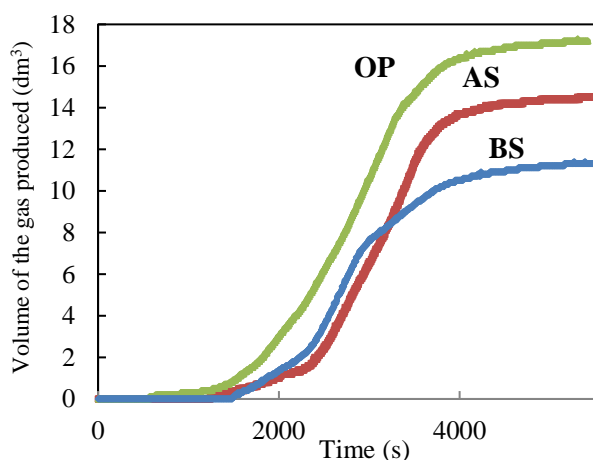

Fig. 1 The dependence of the volume of the pyrolysis gas produced on time (degassing course). OP – orange-peel; AS – apricot-stones; BS – birch-sawdust

FTIR analyses of the incoming biowaste were carried out on a Protégé 460 E.S.P. Spectrometer, Thermo Nicolet Instruments Co., Madison, USA, using a KBr technique. The difference FTIR spectra were acquired regarding the work [12].

During the pyrolysis, the values of the temperature, pressure and volume of the pyrolytic gas were continuously recorded; simultaneously, CO, CO_2, and methane concentrations in the pyrolysis gas were recorded by a continuously working infrared analyser (Teledyne Analytical Instruments, Model 7500).

Analyses of the total gas were performed by gas chromatography with flame ionization and thermal conductivity detection on two Agilent Technology 6890N gas chromatographs. O_2, N_2, and CO were analyzed on a HP-MOLSIV capillary column (40 °C) with helium as carrier gas (5 cm^3/min) using TCD; methane and other hydrocarbons then on a GS-Gaspro capillary column (60 °C) with nitrogen as carrier gas (20 cm^3/min) using FID (air 400 cm^3/min, H_2 30 cm^3/min, N_2 20 cm^3/min); CO_2 on the GS-Gaspro column (40 °C) with helium as carrier gas (5 cm^3/min) using TCD; and hydrogen on an HP-5 capillary column (40 °C) with nitrogen as carrier gas (7 cm^3/min) using TCD.

From the liquid phase, water was removed by azeotropic distillation with n-hexane, bio-oil was thus obtained. Because of its polar character, this oil always contains residual water (~1 wt.%), which is its integral part. Bio-oil composition (rel.%) was determined using the capillary GC method on a Hewlett Packard HP 6890 chromatograph. This gas chromatograph was equipped with a DB XLB capillary column of a length of 30 m and a diameter of 0.25 mm. The carrier gas was helium. For the first minute, the column was maintained at a temperature of 50 °C, after which the temperature was increased to 280 °C with a temperature gradient of 10 °C/min; the following dwell at 280 °C was of 6 min.

2.3. Combusted materials

The materials selected for combustion were the same as those for pyrolysis. Before combustion, the biowastes and the comparative biomass were adjusted like before pyrolysis. As the result of combustion, white ashes were obtained. These resulting ashes were analysed by an X-ray quantitative analysis (see below).

2.4. Combustion conditions and ash analysis

Samples of a weight of around 500 g were combusted in air in ceramic bowls in a muffle furnace, which was heated from room temperature to 1000 °C at a heating rate of 10 °C/min, with a thirty-minute dwell at this final temperature. The elemental composition of the ashes obtained was then determined by a standard-less X-ray analysis, while the powder samples were fixed on a Cu-tape and then analysed by an EDS Silicon Drift Detector Apollo X, EDAX Inc. [10].

3. Results and discussion

The pyrolysis of both types of biowaste and comparative biomass under the given conditions provided products whose yield and composition depended mainly on the character of the pyrolysed material. Based on the product masses determined, mass balance was performed (Table 2). While the bio-oils yields and the yields of water were quite different, pyrolysis gas yields were comparable; solid carbonaceous residue yields were comparable, too. More in details, it arises from the Table 2 that (a) the solid carbonaceous residue yield was comparable in all the cases (27–29 wt.%), (b) the highest bio-oil yield was achieved through apricot-stones pyrolysis (36 wt.%), in contrast, the lowest yield was obtained by orange-peel pyrolysis (only ~6 wt.%), (c) the reaction water yield was relatively very high at orange peel (38 wt.%), and (d) the gas yields from birch sawdust and apricot stones were similar (15–16 wt.%), the gas yield from orange-peel pyrolysis was slightly higher (18.5 wt.%). The losses were acceptable, in the range of 9–11 wt.%.

Table 2 Mass balance of biowastes and comparative biomass pyrolyses (wt.%). For symbols see Table 1

	Solid residue	Bio-oil	Water	Gas	Losses
BS	28.8	23.0	23.8	15.6	8.8
OP	27.0	5.6	37.6	18.5	11.3
AS	28.3	36.1	11.1	15.1	9.4

The low yield of bio-oil from orange peel accompanied by a relatively high amount of reaction water is attributable to the higher polysaccharide component and the lower lignin contents in orange peel in comparison with those in apricot stones and birch sawdust. The decomposition of orange peel then produces fewer phenols, which are quantitatively the key component of bio-oils

[13] and aromatics, and more reaction water. The lower content of lignin in orange peel in comparison with apricot stones is indicated by the difference FTIR spectra (Figs. 2 and 3), from which lignin was subtracted and the resulting subtraction spectra compared. It is evident from the comparison that the band of intermolecular hydrogen bond in cellulose (at 3292 cm^{-1}) is insignificant in the case of apricot stones (Fig. 3), in contrast to the orange-peel spectra, where a hydrogen bonding band (at 3331 cm^{-1}) is quite broad (Fig. 2). It may be inferred from this that orange peel contains more of the polysaccharide component at the expense of the lignin component, and therefore its predisposition for the formation of phenols and aromatics (and subsequently oil) is lower than in the case of apricot stones, while its predisposition for the formation of reaction water is significantly higher as compared with that of apricot stones. As a result, the orange-peel pyrolysis produces less bio-oil and significantly more water than apricot-stones one.

The produced bio-oils were characterised by means of elemental analysis and higher heating value (Table 3). Table 3 indicates that the carbon content in the bio-oils obtained was almost the same, also hydrogen contents were very similar; contrary, the contents were different in the case of nitrogen and sulphur. As the higher heating value of the bio-oils was ca 30–32 MJ/kg, they could be used as heating oils. However, these bio-oils may also be a source of valuable substances, which may be further isolated from them. The comparative GC analyses and a class analysis (Table 4) proved aldehydes and ketones, organic acids and esters (while a significant portion of fatty acid esters), further phenols and aliphatic and aromatic hydrocarbons (one- and two-ring aromatics) while the shares of phenols and esters was the highest.

On the whole, the comparative composition of the bio-oils obtained, illustrated in Table 4, shows their potential use for production of organic chemicals.
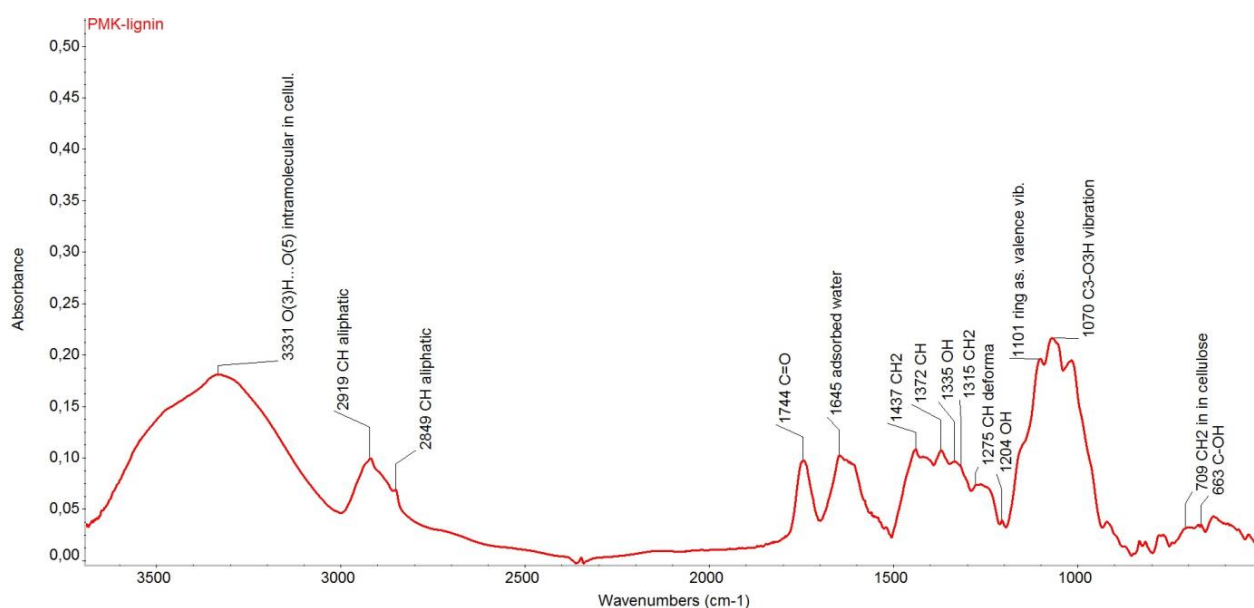

Fig 2 The difference FTIR spectrum of orange peel (after lignin subtraction from the orange peel spectrum)
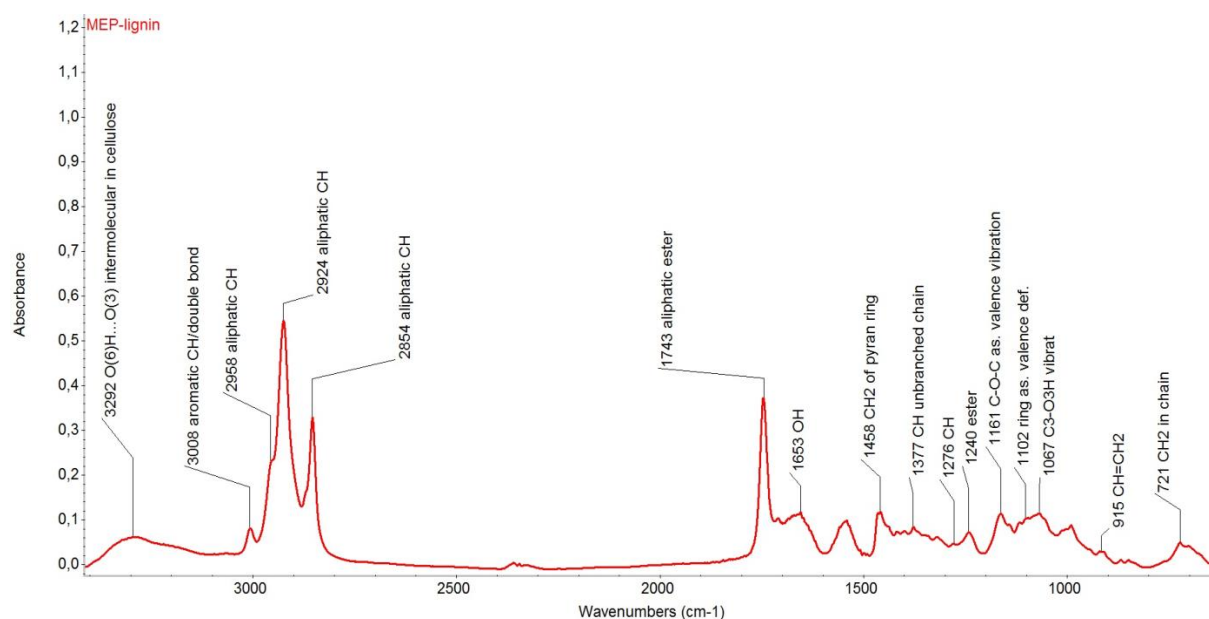
Fig. 3 The difference FTIR spectrum of apricot stones (after lignin subtraction from the apricot-stones spectrum)

Table 3 Elemental analysis of bio-oils obtained and their higher heating values. For symbols see Table 1

	Elemental analysis (wt.%)					HHV (MJ/kg)
	C	H	N	S	O_{dif}	
BS	69.39	8.12	0.52	0.23	21.77	31.71
OP	65.79	8.16	1.67	0.69	23.69	30.13
AS	66.06	8.53	1.66	0.05	23.70	31.16

Table 4 The comparative composition of bio-oils from the GC analysis and class analysis (rel.%). For symbols see Table 1

	Aldehydes and ketones	Organic acids	Esters	Phenols	Lower hydrocarbons and one-ring aromatics	Higher hydrocarbons and two-ring aromatics
BS	20.39	5.65	21.55	44.93	4.60	3.42
OP	24.36	20.28	28.76	25.50	1.10	0.00
AS	9.12	6.32	32.88	28.42	21.58	1.68

The resulting solid carbonaceous residues of pyrolysis were characterized by proximate and ultimate analyses and higher heating value (Table 5).

Table 5 The composition and properties of the solid carbonaceous pyrolysis residues. For symbols see Table 1

	Proximate analysis (wt.%)			Ultimate analysis (wt.%)					HHV (MJ/kg)
	W	A	VM	C	H	N	S_o	O_{dif}	
BS	2.29	8.45	14.26	86.82	2.67	1.30	0.06	9.15	32.94
OP	3.73	7.49	13.32	88.38	2.75	2.50	0.09	6.29	33.44
AS	2.18	2.99	8.65	91.45	2.84	2.05	0.04	3.63	34.97

The values in Table 5 prove that the ash content was acceptable in all the cases and the higher heating value of the solid pyrolysis residues was relatively high, 33-35 MJ/kg. The higher heating value of the solid carbonaceous residue from birch sawdust is comparable with the low heating value of brown coal (25–32 MJ/kg); the solid residues from both the orange peel and the apricot stones exhibited higher heating values, comparable with those of bituminous coal. The ash content in the solid residue from the apricot stones was 2–3 times lower than that in the case of birch sawdust and orange peel. Further, it is evident from a comparison of the sulphur values in Tables 3 and 5 that during the pyrolysis the sulphur contained in the incoming materials was transferred mainly into volatile products, not into solid residue.

The composition of the resulting gas is shown in Table 6. It is evident from the table that the main components are carbon oxides in the total representation of 71-73 vol.%, which results from the high oxygen content in the incoming materials (Tab. 1). It further arises from Table 6 that orange peel pyrolysis produced the lowest amount of carbon monoxide and more carbon dioxide than in the other cases. Moreover, the gas obtained from the orange peel contained, in comparison with the other components, the highest amount of hydrogen and the smallest amount of methane. The lower heating value of the total gas was 11–14 MJ/m³. Considering these values, the gas may find application as an energetic gas after a deeper conversion procedure.

With the bio-wastes studied, the generation of individual gases differed (Figs. 4–6).

Table 6 The composition of the total gas from biomass and biowastes pyrolyses. LHV – lower heating value. For other symbols see Table 1

	CH_4	ΣC_2-C_4	N_2	CO	CO_2	H_2	LHV
	(vol. %)						(MJ/m^3)
BS	15.43	3.92	1.20	29.2	43.4	6.84	13.22
OP	13.50	4.25	0.69	18.0	55.2	8.42	11.08
AS	18.67	4.63	0.60	28.0	43.4	4.70	14.17

In the case of the apricot stones (Fig. 5), the generation of both the majority carbon dioxide and minor components (CH_4 and CO) approached the generation of these components from comparative biomass (Fig. 4). With orange peel (Fig. 6), the development of CO_2 was substantially more intensive and the development of CH_4 and CO less intensive in comparison with that of apricot stones. The character of biowaste, reflected in the elemental composition (Tab. 1), thus determines the generation of individual gases such that biowaste containing a higher amount of oxygen, in this case orange peel, also produces more CO_2. The concentrations of CH_4 and CO in the gas are then adequately lower. CO_2 dominated in the generation of the total gas (Figs. 4–6) and it was its generation that determined the utility properties of the total gas.
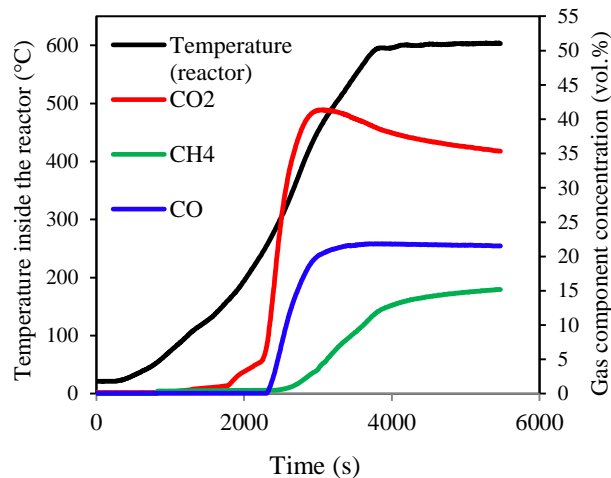

Fig. 4 The generation of the main gaseous components during the pyrolysis of birch sawdust in dependence on time and temperature inside the reactor

The ashes from the combustion of biowastes and comparative biomass and the use them for fertilisation were further investigated.
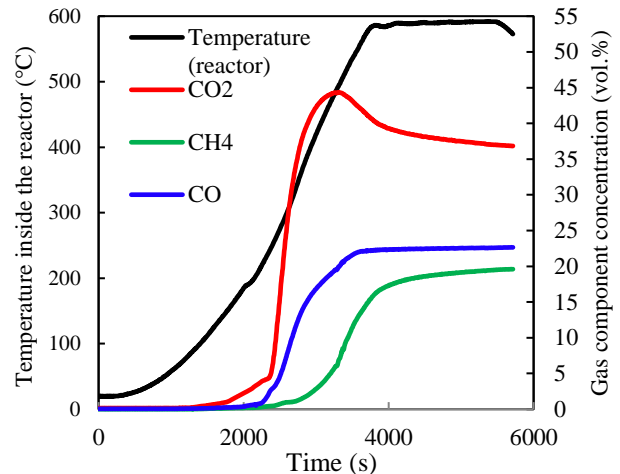

Fig. 5 The generation of the main gaseous components during apricot stones pyrolysis in dependence on time and the temperature inside the reactor
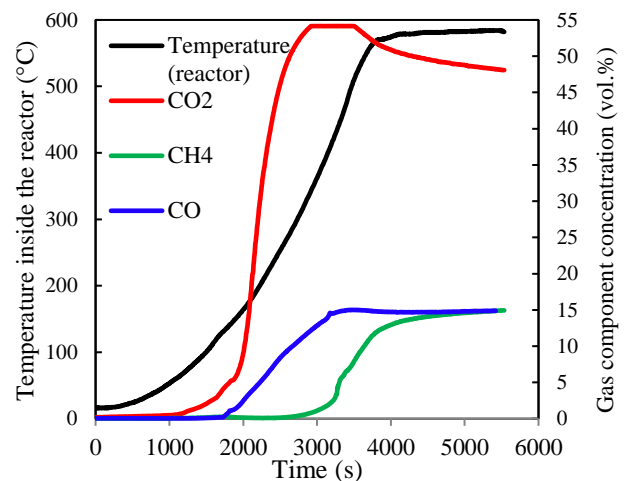

Fig. 6 The generation of the main gaseous components during orange peel pyrolysis in dependence on time and the temperature inside the reactor

The ashes obtained were considered as fertilisers, based on the content of essential elements: main biogenic elements (N, P, K), secondary biogenic elements (Ca, S, Mg) and trace elements useful for fertilisation of agricultural lands. The complete composition of ashes from laboratory combustion by X-ray analysis is shown in Table 7. In comparison with birch sawdust, the orange peel and apricot stones ashes contained higher amount of phosphorus and, in case of apricot stones, nitrogen as well; they also contained more K but less calcium.

Table 7 The elemental composition of the ashes studied; (-) not identified. For symbols see Table 1

Ash from	C	O	Na	Ca	K	Mg	Fe	Al	Si	P	N	S
BS	4.46	29.66	0.86	47.15	10.37	2.66	0.82	0.73	1.36	1.25	(-)	0.70
OP	4.36	26.40	1.05	34.90	24.06	1.54	(-)	(-)	(-)	5.64	(-)	2.05
AS	7.15	26.18	0.53	6.53	31.29	8.03	(-)	(-)	(-)	17.11	2.87	0.31

Apricot stones ash contained even less calcium, but it had a relatively high content of Mg, even 8%. In the ashes from the biowastes studied, no trace elements were discovered, not even Fe like in the comparative biomass.

The high amounts of P and K in the ashes from biowastes are clearly a positive phenomenon, just like the 3% of N found in the case of apricot stones and the content of Ca and S in the case of orange peel. In the case of magnesium, however, it depends on its form and extractable content.

The carbonates form of the fertiliser ($MgCO_3$) acts more slowly than the sulphate ($MgSO_4$) or chloride ($MgCl_2$) forms, where Cl is problematic as well. A favourable amount of Mg in soil is around 200 ppm Mg. When the soil contained a high amount of Mg (e.g. above 2,000 ppm), Mg became slightly toxic. At 5000 ppm, plants (e.g. tea tree) had problems with the absorption of Ca, or K [14]. The use of ash with a relatively high content of magnesium hence must be carefully considered. Generally speaking, orange peel and apricot stones ashes are more suitable for the preparation of fertilisers for agricultural lands than as fertilisers as such.

4. Conclusions

Pyrolysis of two types of biowaste that are hard to treat, apricot stones and orange peel, and comparative biomass, birch sawdust, have been studied. The pyrolysis of these materials has produced gas with a lower heating value of 11–14 MJ/m^3, which may be used as energetic gas, but after a conversion procedure. The generation of the pyrolysis gas was influenced by the character of the biowaste, with the generation of CO_2 being dominant. The mass balance has shown that the given conditions lead to the creation of 27–29 wt.% of solid carbonaceous residue, which may be further used as auxiliary fuel. The obtained bio-oils exhibited an acceptable higher heating value of 30–32 MJ/kg and can subsequently be used as heating fuels. Considering the broad spectrum of substances present in bio-oils (aldehydes and ketones, organic acids and esters, phenols and aliphatic and aromatic hydrocarbons, with the share of phenols and esters being the highest), they may also be used as a source of chemicals.

Ashes from the types of biowastes studied can be used for the preparation of fertilisers for agricultural lands, because they contain significant amounts of essential elements: phosphorus, potassium and magnesium as well as calcium and sulphur.

Acknowledgments

5. References

1. Diebold J.P., Bridgwater A.V.: 1997, Overview of fast pyrolysis of biomass for the production of liquid fuels. In: Developments in Thermochemical Biomass Conversion, Springer Netherlands, pp. 5–23.

2. Dinesh M., Pittman C.U., Jr., Steele P.H.: 2006, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. Energy & Fuels 20, 848–889.

3. Dufour A., Girods P., Masson E., Rogaume Y., Zoulalian A.: 2009, Synthesis gas production by biomass pyrolysis: Effect of reactor temperature on product distribution. International Journal of Hydrogen Energy 34, 1726–1734.

4. Hornung U., Schneider D., Hornung A., Tumiatti V., Seifert H.: 2009, Sequential pyrolysis and catalytic low temperature reforming of wheat straw. Journal of Analytical and Applied Pyrolysis 89, 145–150.

5. Yaman S.: 2004, Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management 45, 651–671.

6. Jílková L., Ciahotný K., Kusý J., Káňa J.: 2011, Kopyrolýza hnědého uhlí a řepkových pokrutin (Co-pyrolysis of Lignite and Rapeseed Cake). Paliva 3, 119–125.

7. Bridgwater A.V. (Ed.): 2001, Progress in Thermochemical Biomass Conversion, Vol. 2, Blackwell Science, London.8. Demirbas A.: 2005, Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Progress in Energy and Combustion Science 31, 171–192.

8. Khan A.A., de Jong W., Jansens P.J., Spliethoff H.: 2009, Biomass combustion in fluidized bed boilers: Potential problems and remedies. Fuel Processing Technology 90, 21–50.

9. Straka P., Náhunková J., Žaloudková M.: 2014, Analysis of unburned carbon in industrial ashes from biomass combustion by thermogravimetric method using Boudouard reaction. Thermochimica Acta 575, 188–194.

10. Straka P., Bičáková O.: 2014, Hydrogen-rich gas as a product of two-stage co-gasification of linite/waste plastics mixtures. International Journal of Hydrogen Energy 39, 10987–10995.

11. Schwanninger M., Rodrigues J.C., Pereira H., Hinterstoisser B.: 2004, Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. Vibrational Spectroscopy 36, 23–40.

12. Branca C., Giudicianni P., Di Blasi C.: 2005, GS/MS characterization of liquids generated from low-temperature pyrolysis of wood, Industrial & Engineering Chemistry Research 42, 3190–3202.

13. Gustafson G. M., Salomon E., Jonsson S.: 2007, Barn balance calculations of Ca, Cu, K, Mg, Mn, N, P, S and Zn in a conventional and organic dairy farm in Sweden. Agriculture, Ecosystems & Environment 119, 160–170.