

LOW-TEMPERATURE TREATMENT OF WASTE PET

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Today, waste plastics represent a promising source both for energy production and chemicals. One way to use their potential is pyrolysis under well-defined conditions. This work presents a suitable method for treatment of waste polyethylene terephthalate (PET) using low-temperature pyrolysis realized by heating rates of $5\text{ }^{\circ}\text{C min}^{-1}$ (slow pyrolysis) or $25\text{ }^{\circ}\text{C min}^{-1}$ (fast pyrolysis) up to final temperature of $400\text{ }^{\circ}\text{C}$. Under these conditions, the valuable products were formed, namely solid fuel with HHV $31\text{--}33\text{ MJ kg}^{-1}$ and liquid mixture containing mainly ethylene glycol and aldehydes. While slow pyrolysis provides mainly solid fuel, ethylene glycol and aldehydes, main products of fast pyrolysis are solid fuel and paraldehyde.

Keywords: PET, Pyrolysis, Ethylene glycol, Aldehyde, Solid fuel

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1. Introduction

Polyethylene terephthalate is a plastic used in everyday life and therefore its waste is considerable and thus problematic. In 2017, more than 3.3 million tonnes of PET bottles were placed in the European market and more than 1.9 million tonnes of those were collected for recycling in the same year [1]; nothing is known about the remaining 1.4 million tons of PET waste. In 2021, global annual consumption of PET packaging is forecast to reach probably ~ 21 million tonnes [2]. With such consumption, there will certainly be considerable waste. It is therefore necessary to consider further treatment methods, as the re-use of waste PET has significant limits which is often not mentioned at all. A viable route of processing seems to be low-temperature pyrolysis providing products with high utility value using a technologically feasible process. This method is newly suggested based on the following literature review of PET disposal.

Incineration is often applied because it solves in a simple way the problems with increasing constraints of landfilling and plastic wastes sorting. But (a) it emits toxic air pollutants (dioxins, furans, polychlorinated biphenyls, mercury) [3, 4], (b) devalues potentially usable substances that could be extracted from PET [5], (c) residues after incineration of PET waste contaminate ground soil by leaching of lead and cadmium [6], (d) PET incineration is not an energy efficient because PET is one of the plastics with the lowest calorific value, $\sim 22\text{ MJ kg}^{-1}$, so, it mainly reduces the volume of waste plastic without any further utility. Thus, more efficient and technologically appropriate methods need to be sought for PET disposal.

Chemical recycling using hydrolysis, glycolysis and methanolysis represents a more sophisticated solution of PET disposal by trying to obtain starting monomers for further use. As these methods are based on reversibility of polycondensation reaction of monomers in question, they can result in total recycling.

- *Hydrolysis.* A strong motivation for the hydrolysis of PET is the possibility of its conversion to the structural

monomers, i.e. terephthalic acid and/or ethylene glycol which will be released under suitable conditions. Masuda et al. [7] successfully decomposed PET in a steam atmosphere yielding terephthalic acid. Authors found that steam accelerated the hydrolysis of PET, yielding terephthalic acid and oxygen-containing compounds (aldehydes and esters) with less than 1% of solid carbonaceous residue. The yield of terephthalic acid $\sim 87\%$ at $\sim 450\text{ }^{\circ}\text{C}$ using a carrier gas containing 70% steam and 30% nitrogen was reached. Using steam, a fluidised bed hydrolysis was also tested [8], while steam was generated by a steam generator at a temperature of $150\text{ }^{\circ}\text{C}$. In the reactor, steam was heated to the desired temperature $400\text{--}500\text{ }^{\circ}\text{C}$. It was found that $60\text{--}72\%$ of stoichiometric terephthalic acid can be obtained back from PET whereas the highest yield, 72%, was obtained at $450\text{ }^{\circ}\text{C}$. Contrary, the yield of ethylene glycol was less than 10% in all experiments, because it mostly reacted with steam water to carbon oxides and hydrogen. Other decomposition products were acetaldehyde and ethene. On the hydrolysis, transition metal oxides have a catalytic effect. A fluidized bed technique was also successfully applied for PET pyrolysis on a fluidized bed plant [9] (see below).

Other study was devoted to waste PET hydrolysis using a 96% commercial sulfuric acid at varying reaction times (5–120 min) [10]. It was found that dissolution of PET in concentrated H_2SO_4 starts in amorphous parts, thus, the amorphous phase is relatively quickly dissolved. (Note: PET is a semi-crystalline polymer; it can be obtained in amorphous or semi-crystalline state; in latter it has both an amorphous regions and crystallites [11].) As the reaction time increases, both the amorphous and crystalline regions dissolve due to cracks and subsequent penetration of acid into the material which causes its complete dissolution and complete hydrolysis of the polymer.

- *Glycolysis.* This method is focused on obtaining a terephthalate monomer. Glycolysis of waste PET granules was carried out in the presence of depolymerization catalysts (zinc acetate, sodium carbonate, sodium bicarbonate, sodium sulphate and potassium sulphate) with an

excess of ethylene glycol (EG) [12]. The high yield about 70% of the monomer bis(2-hydroxyethyl terephthalate) was obtained with zinc acetate and sodium carbonate at 196 °C at a large excess of glycol. Namely the latter salt could indeed act as an effective and environment-friendly catalyst. In this connection, the optimal conditions for glycolysis of PET were suggested [13]. A remarkably high yield of above monomer (75.7%) was obtained at the optimal operating conditions (temperature, reaction time, EG/PET and NaHCO₃/PET mass ratios).

- *Methanolysis.* Both desired monomers can be obtained by methanolysis. The PET flakes methanolysis at 200 °C in methanol with an aluminium triisopropoxide catalyst was carried out [14]. This procedure yielded dimethyl terephthalate and ethylene glycol in 64% and 63% predicted yields, respectively. The yields were increased using a toluene/methanol solvent with 20–50 vol.% toluene, maximum yields (88% of predicted dimethyl terephthalate and 87% of predicted ethylene glycol) were obtained at 20 vol.% toluene. The reason is that under given conditions, the yields of mentioned monomers strongly depend on the solubility of PET and following oligomerization. In the toluene/methanol solvent, most PET depolymerized to oligomers because this mixed solvent effectively accelerates their formation due to swelling of PET crystals.

Another approach is to use a supercritical methanol. Yang et al. [15] carried out a methanolysis depolymerization of PET wastes in temperature range of 250–270 °C and pressures of 8.5–14.0 MPa while the weight ratios of methanol/PET were 3–8. Dimethyl terephthalate as solid product and ethylene glycol in methanol were obtained. The optimal depolymerization conditions were found at temperature of 260–270 °C, pressure 9.0–11.0 MPa, and the methanol/PET ratio 6–8.

Overall, chemical recycling methods can lead to complete recycling, but they require intensive cleaning of PET waste, which is often not mentioned by the authors. However, this is evident from the work of Brems et al. [16], therefore, authors suggest pyrolysis as the most promising method.

Pyrolysis. Pyrolysis occur within a 410–460 °C range at 10 °C min⁻¹ [16]. Girija et al. [17] report 390–450 °C, according to our measurements it is 380–440 °C. According to [16], often, the gaseous products represent ~16–18 wt.%; further, the amounts of condensables and carbonaceous residue depend on the operating mode, while slow pyrolysis produces up to 24 wt.% of carbonaceous residue; major condensable components are benzoic acid and vinyl benzoate, mono- and divinyl terephthalates, and benzene. Pyrolysis can be carried out in fixed or in fluidized beds. Anděl et al. [18] propose two-product pyrolysis in fixed bed under specific conditions to obtain a mixture of terephthalic and benzoic acids in the ratio of 10:1 and a solid carbonaceous residue, which can then be used as an active carbon. The carbonaceous residue can also be upgraded as a carburizing agent for steel industry [19].

Brems et al. [16] proposed that the optimal reactor for PET pyrolysis is either the bubbling or circulating fluidized bed. Yoshioka et al. [9] carried out pyrolysis of various PET materials in a fluidized bed plant in the temperature range of 510–730 °C. Practically, only gas and solid products were obtained. The gas yield was mainly 38–49 wt.% whereas the gas mixture consisted mainly of CO₂ and CO. Further, the solid organic residues resulted from pyrolysis. Their amount increased strongly with temperature, while 5 wt.% was found at a temperature of 510 °C, but at 730 °C ~40 wt.% was formed. With increasing temperature, the amount of oxygen containing compounds decreased due to the decomposition of terephthalic and benzoic acids. So, at 510 °C, terephthalic and benzoic acids, monomethyl terephthalate and carbon oxides are the main products. With increasing temperature, acids disappear by forming more carbonization products, which reach ~40 wt.% at 730 °C.

For PET depolymerization, a technology based on use of microwave heating was developed. It is characterized by low energy consumption and high purity of obtained terephthalic acid and ethylene glycol. A proposed procedure was tested on a pilot plant with capacity in the range of 1–10 kg h⁻¹ waste PET bottles [20]. Another possible use of waste PET is reported by Havelcová et al. [21] who studied the effect of PET addition to coking blends while sub-bituminous coal was co-processed. It was found that the properties of coke and gas changed significantly at 20% of the waste PET in the coal charge.

It is clear from the presented overview that pyrolysis under defined conditions is a promising method of waste PET processing and that it needs to be further addressed. In our case, we focused on obtaining of solid fuel with high heating values, ethylene glycol for possible use in antifreeze and anticorrosion fluids, and aldehydes as useful chemicals.

The study of low-temperature PET pyrolysis requires appropriate analytical methods. With respect to the work of Kurokawa et al. [14] it can be assumed that PET degradation will proceed in three steps. In the first one, the chains length is shortened only. Then, in the second step, the shortened chains are depolymerized to oligomers on random positions of the polymer chain. The third step includes splitting of oligomers to monomers. Therefore, it is necessary to expect mixtures of large and small molecules and it is appropriate to choose a combination of molecular spectroscopy and gas chromatography methods. In our case, FTIR spectroscopy and capillary chromatography were selected.

2. Experimental

2.1. Material

Waste PET from various collection areas in the Czech Republic was firstly processed using cutting mill into flakes with a size of several mm, which were then spread over an area, and samples ~100 g were prepared by random selection. No other processing of the material was performed and the samples were subjected to heating

under well-defined conditions. The basic characteristic of the PET used was obtained by differential scanning calorimetry on a Perkin-Elmer Pyris DSC 7 analyzer. Its melting point was of 249 °C. Based on the work [11], it was, highly probably, a semi-crystalline polymer with a significant proportion of amorphous phase.

2.2. Methods

100 g PET samples were pyrolyzed in an own atmosphere on a fixed-bed laboratory unit (Fig. 1, 1b – right) consisting of vertical quartz reactor placed in an electric resistance furnace controlled by a programmable heating system, a gas holder, collecting flask and ethanol-cooled condensers (ethanol -10 °C) (Fig. 1, 1a – left), and

continuously working sensors of temperature field, pressure and gas volume. A capture of all products (total gas, liquid fraction and solid carbonaceous residue) was secured. The samples were heated at 5, 10 and 25 °C min⁻¹ to final temperatures of 360–400 °C. For the first data on the thermal behavior of PET, randomly selected samples were heated at a conventional rate of 10 °C min⁻¹ to a final temperature of 400 °C. Other tested samples were firstly heated with the rate of 40 °C min⁻¹ from room temperature to 200 °C and then at heating rate 5 °C min⁻¹ or 25 °C min⁻¹ to the final temperatures of 360, 380 and 400 °C. All pyrolysis processes performed were described by course of temperature, an evolution of gas and a mass balance.

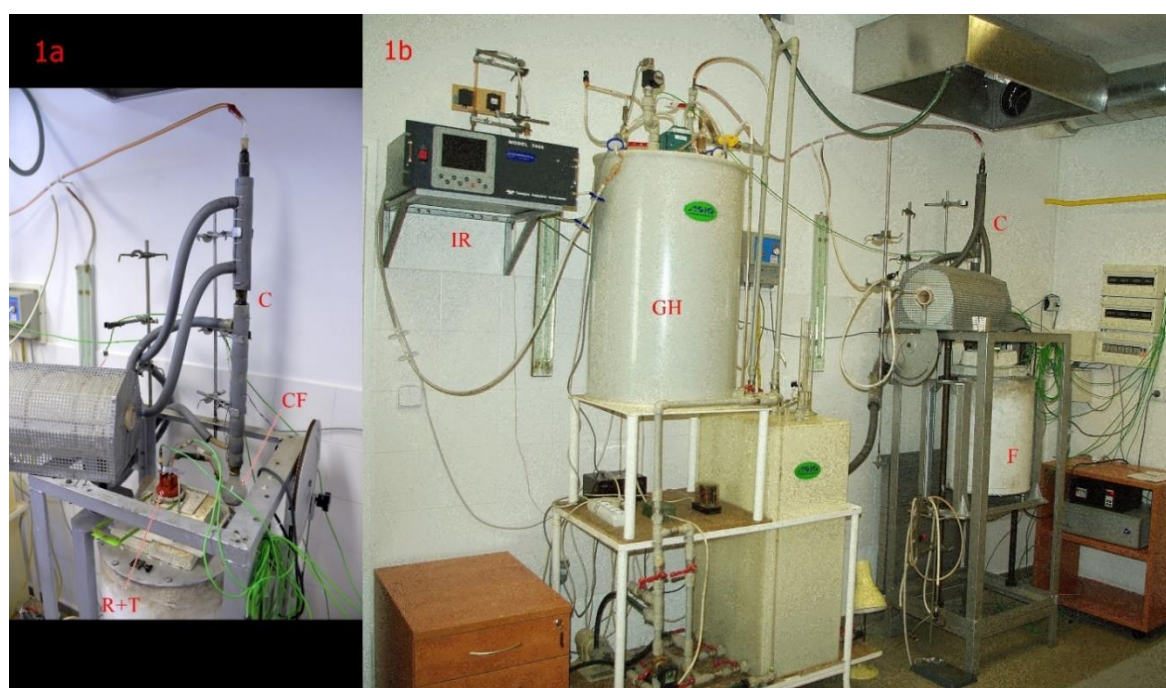


Fig. 1 Laboratory unit for PET pyrolysis. **1b**: F – furnace with vertical quartz reactor, C – condensers, GH – gasholder; IR – continuous infrared gas analyzer. **1a**: CF – collecting flask (first cooling); C – two condensers (second cooling), (third cooling to room temperature takes place in the gasholder); R+T – quartz reactor output and thermocouples

The total gas analysis was performed by a GC method using FID and TCD on two Agilent Technology 6890N gas chromatographs. O₂, N₂ and CO were analyzed on an HP-MOLSIV capillary column (40 °C) with He as carrier gas (5 cm³ min⁻¹) using TCD; methane and C₂–C₄ hydrocarbons then on a GS-Gaspro capillary column (60 °C) with N₂ as carrier gas (20 cm³ min⁻¹) using FID (air 400 cm³ min⁻¹, H₂ 30 cm³ min⁻¹, above N₂); CO₂ then also on a GS-Gaspro capillary column (40 °C) with He as carrier gas (5 cm³ min⁻¹) using TCD. Hydrogen was analyzed on an HP-5 capillary column (40 °C) with N₂ as carrier gas (7 cm³ min⁻¹) using TCD.

FTIR analyses of obtained liquid fractions were carried out on a Protégé 460 E.S.P. Spectrometer, Thermo

Nicolet Instruments Co., Madison, USA, using an ATR technique. Minor components in these mixtures were determined on an Agilent Technologies 6890 gas chromatograph with an MSD 5975 mass spectrometer; an Agilent DB XLB capillary column with a length of 30 m and a diameter of 0.25 mm was used, the carrier gas was He. The temperature program was as follows. The column was maintained at 50 °C for the first minute, then the temperature increased from 50 °C to 300 °C with a temperature gradient of 10 °C min⁻¹; after reaching this temperature, the delay was 6 min.

Solid carbonaceous products obtained were characterized by proximate and ultimate analyses, further by lower and higher heating values (LHV and HHV, resp.).

3. Results and discussion

Pyrolysis at a conventional heating rate $10\text{ }^{\circ}\text{C min}^{-1}$ and a final temperature $400\text{ }^{\circ}\text{C}$ showed a mass balance of 67% solid residue, 23.5% liquid mixture, 8% gas and 1.5% losses. From the [9] and [16] it follows that formation of liquid products and a solid residue strongly depends on the final temperature; further, the heating rate is a key parameter of PET decomposition. Therefore, final temperatures 360, 380 and $400\text{ }^{\circ}\text{C}$ and heating rates of $5\text{ }^{\circ}\text{C min}^{-1}$ (pyrolysis time 37–45 min, slow pyrolysis) and $25\text{ }^{\circ}\text{C min}^{-1}$ (pyrolysis time 11–13 min, fast pyrolysis) were selected for experiments. (Note: classification of heating rates (w) is generally quite different. In our case, $w\text{ }10\text{ }^{\circ}\text{C min}^{-1}$ (often used in TGA) was considered as conventional, w significantly higher than $10\text{ }^{\circ}\text{C min}^{-1}$ as fast and that lower than $10\text{ }^{\circ}\text{C min}^{-1}$ as slow.)

From the achieved results, the mass balance was first calculated (Table 1).

Table 1 Mass balance (wt.%) of waste PET pyrolysis at heating rates of 5 and $25\text{ }^{\circ}\text{C min}^{-1}$ (over $200\text{ }^{\circ}\text{C}$) and final temperatures of 360, 380 and $400\text{ }^{\circ}\text{C}$

No.	$^{\circ}\text{C min}^{-1}$	$^{\circ}\text{C}$	Solid residue	Liquid fraction	Gas	Losses
1		360	90.2	1.7	2.2	6.0
2	5	380	80.2	9.3	3.2	7.3
3		400	47.4	30.2	14.3	8.1
4		360	89.0	5.3	3.1	2.7
5	25	380	78.8	11.5	4.9	4.9
6		400	39.7	46.7	13.3	0.3

With slow pyrolysis, 80–90% of solid residue was obtained at final temperatures 360 and $380\text{ }^{\circ}\text{C}$, but yield of liquid fractions was 2–9% only. Contrary, at $400\text{ }^{\circ}\text{C}$, 30% liquids and 47% of solid phase were reached. As shown in Tab. 1, the fast pyrolysis provided similar results. Since in both cases, at $400\text{ }^{\circ}\text{C}$ also the gas yield increased

compared with 360 and $380\text{ }^{\circ}\text{C}$, it can be said that the decisive factor for the production of volatiles and products distribution was the final temperature of decomposition. In this connection, it must be underlined that the losses were acceptable, 0–8%.

From practical point of view, the LHV and HHV of the solid residue obtained at different final temperatures and heating rates are significant. These values together with proximate and ultimate analyses are summarized in Tables 2 and 3. Water, ash and sulfur contents were, as expected, very low and negligible, resp. HHV (a.r.) were 23.5 and 24 MJ kg^{-1} for solids from slow pyrolysis at 360 and $380\text{ }^{\circ}\text{C}$, resp., and 24.2 and 23.6 MJ kg^{-1} for those from fast pyrolysis at the same temperatures. In contrast, at $400\text{ }^{\circ}\text{C}$ they were much higher in both cases. If we consider that the HHV of waste PET is usually between 21.9– 24.7 MJ kg^{-1} [22], then the values achieved at 360 and $380\text{ }^{\circ}\text{C}$ at both heating rates were comparable to those for waste PET, but the values at $400\text{ }^{\circ}\text{C}$ were significantly higher, 31.3 MJ kg^{-1} . The same can be said about LHV (Tables 2 and 3). Thus, both slow and fast pyrolysis showed a significant improvement in solid fuel over the starting PET waste. The reason is a substantial increase in the amount of carbon and a decrease in oxygen in solids at the final pyrolysis temperature of $400\text{ }^{\circ}\text{C}$ (Tabs. 2 and 3).

To evaluate the liquid fractions, the yield, composition and amount of a key component were considered. In our case, the key component was ethylene glycol, the minor components were aldehydes, benzoic acid and its derivatives, acetic acid and oxo compounds (Table 4). Satisfactory yield of the liquid fraction was achieved only at $400\text{ }^{\circ}\text{C}$ (Table 1) with both heating rates, but ethylene glycol was recorded only with slow pyrolysis. FTIR spectroscopy in the range of $3700\text{--}2500\text{ cm}^{-1}$ was used for the detection of ethylene glycol and OH groups [23,24]; spectra are shown in Fig. 2, separation and deconvolution of $3700\text{--}3000\text{ cm}^{-1}$ band in Fig. 3.

Table 2 Proximate and ultimate analyses (wt.%), LHV and HHV of obtained solid carbonaceous residue (the heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ and final temperatures of 360, 380 and $400\text{ }^{\circ}\text{C}$). FC – fixed carbon, VM – volatile matter, a.r. – as received

	360 $^{\circ}\text{C}$		380 $^{\circ}\text{C}$		400 $^{\circ}\text{C}$	
	a.r.	daf	a.r.	daf	a.r.	daf
Water	0.49	-	0.48	-	1.03	-
Ash	0.30	-	0.16	-	0.91	-
FC	13.58	-	20.49	-	63.50	-
VM	85.63	-	78.87	-	34.56	-
FC+VM	99.21	100.00	99.36	100.00	98.06	100.00
H	4.23	4.26	3.83	3.85	3.83	3.90
C	62.97	63.48	64.45	64.87	80.72	82.32
N	0.02	0.02	0.02	0.02	0.17	0.17
O	31.99	32.24	31.06	31.26	13.35	13.61
S(org)	0.00	0.00	0.00	0.00	0.00	0.00
HHV (MJ/kg)	23.54	23.73	23.65	23.80	31.28	31.90
LHV (MJ/kg)	22.60	22.80	22.80	22.96	30.42	31.04

Table 3 Proximate and ultimate analyses (wt.%), LHV and HHV of obtained solid carbonaceous residue (heating rate of 25 °C min⁻¹ and final temperatures of 360, 380 and 400 °C). For symbols see Table 2

	360 °C		380 °C		400 °C	
	a.r.	daf	a.r.	daf	a.r.	daf
Water	0.57	-	0.61	-	1.87	-
Ash	0.21	-	0.28	-	1.66	-
FC	14.73	-	21.38	-	64.87	-
VM	84.49	-	77.73	-	31.60	-
FC+VM	99.22	100.00	99.11	100.00	96.47	100.00
H	4.44	4.48	3.98	4.02	3.97	4.12
C	63.59	64.09	63.83	64.40	80.01	82.94
N	0.19	0.19	0.14	0.14	0.15	0.15
O	30.75	30.99	30.90	31.18	12.02	12.46
S(org)	0.25	0.25	0.26	0.26	0.32	0.33
HHV (MJ/kg)	24.15	24.34	23.64	23.85	31.27	32.42
LHV (MJ/kg)	23.17	23.36	22.76	22.98	30.36	31.52

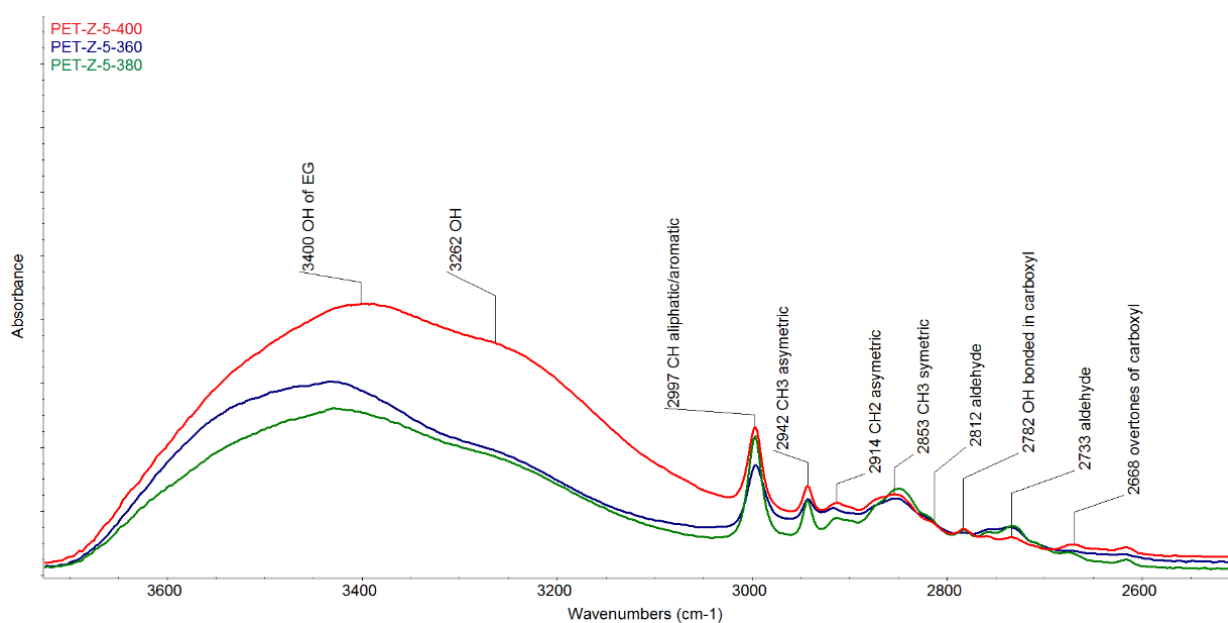


Fig. 2 FTIR spectra of the liquid fractions in the range of 3700–2500 cm⁻¹. A significant band at 3400 cm⁻¹ belongs to resulting ethylene glycol [24]. (Slow pyrolysis, the final temperatures: 360 °C – blue line, 380 °C – green line, 400 °C – red line). Assignment (cm⁻¹): 3400 – OH in ethylene glycol; 3262 – OH in water; 2997 – CH in aliphatics and/or aromatics; 2942 – CH₃, asymmetric stretching; 2914 – CH₂, asymmetric stretching; 2853 – CH₃, symmetric stretching; 2812 – aldehyde; 2782 – OH in carboxyl; 2733 – aldehyde; 2668 – overtones in carboxyl

Further, the minor components in liquid fraction resulted from slow pyrolysis at 400 °C were determined. The results are shown in Table 4. It is obvious that practically only oxygen-containing compounds were detected in the liquid fraction while aldehydes were prevailing. Therefore, considering that at 400 °C (a) the proportion of the liquid fraction substantially increased compared to those at 360 and 380 °C (Table 1), (b) the oxygen content in the solid phase was significantly reduced compared to that at 360 and 380 °C (Tables 2 and 3), (c) mainly oxygen-containing organic compounds were identified in the liquid fraction, and (d) ethylene glycol was identified in

FTIR spectra in significant amount, then it can be concluded that at temperature of 400 °C a distinctive different degradation of PET occurred leading to the formation of ethylene glycol, aldehydes and minor oxygen-containing compounds. Similar phenomena were observed at both heating rates, but ethylene glycol was formed only during slow pyrolysis while diols were identified in liquid fraction from fast pyrolysis, namely 1,1-ethanediol, 1,3-butanediol and further 3,6-dimethyloctane-4,5-diol (GC-MS method). Moreover, a significant amount of paraldehyde was found in the liquid mixture resulting from fast pyrolysis, more than 19 wt.%.

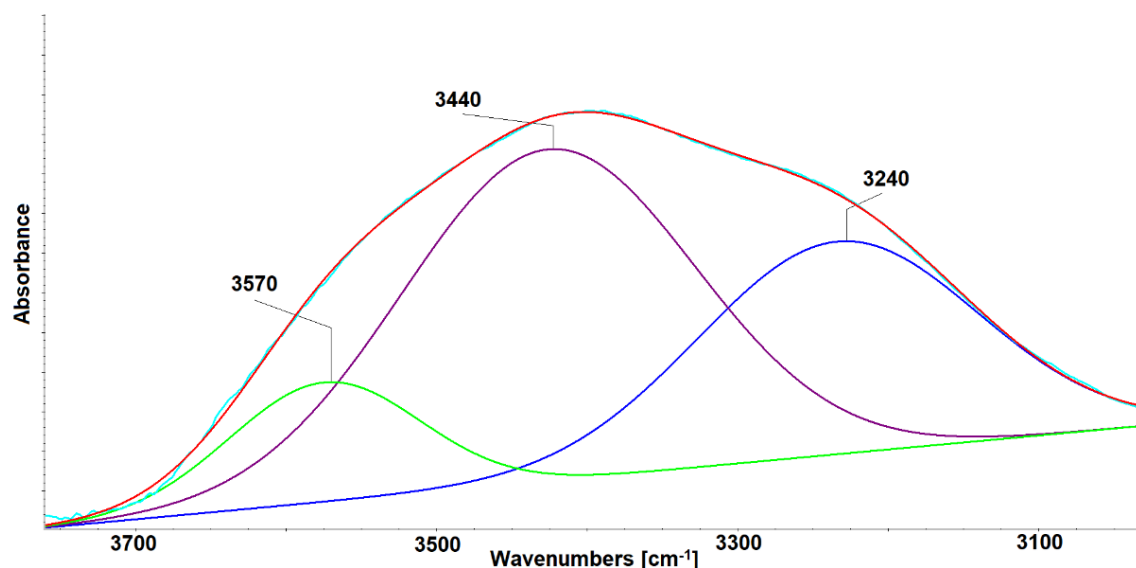


Fig. 3 Separation and deconvolution of the 3700–3000 cm^{-1} band. 3570 cm^{-1} – free OH, 3440 cm^{-1} – O-H stretch in ethylene glycol [24], 3240 cm^{-1} – O-H stretch in COOH

Table 4 Minor organic compounds in the liquid fraction from PET pyrolysis (5 $^{\circ}\text{C min}^{-1}$ over 200 $^{\circ}\text{C}$, final temperature 400 $^{\circ}\text{C}$)

Group of compounds	Compound	wt.%
Aldehydes	acetaldehyde	5.20
	paraldehyde	21.79
benzoic acid and its derivatives	benzoic acid	1.04
	ethyl ester benzoic acid	0.05
	4-methyl benzoic acid	0.14
	4-ethyl benzoic acid	0.16
	4-acetyl benzoic acid	0.24
Acids	acetic acid	0.44
	phenol	0.02
oxo compounds	1-phenyl-1,2-propanedione	1.41
	acetone	0.87
	other oxo compounds	0.80
Total		32.16

The mass balance further showed that also the gas yield increased at 400 $^{\circ}\text{C}$ (Table 1). Therefore, it is clear that the increase in temperature promotes the deep decomposition of PET accompanied by the formation of volatile products. The dominant components of the released gas were carbon oxides, with smaller amounts of ethylene (Tabs. 5 and 6). Tables 5 and 6 show that the gas composition depends on the final temperature. Thus, at final temperature of 400 $^{\circ}\text{C}$, the amount of gas produced increased compared to 360 and 380 $^{\circ}\text{C}$ and its composition changed while the amounts of carbon oxides increased and those of hydrogen and hydrocarbons C_{1-4} decreased (Tab. 7). These data suggest the increased decomposition of terephthalic acid with increasing temperature during the PET degradation.

Table 5 Composition of gas from slow pyrolysis of waste PET at different final temperatures

	360 $^{\circ}\text{C}$	380 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$
methane	3.45	1.91	1.87
ethylene	5.81	6.04	4.01
ethane	0.28	0.23	0.08
propylene	0.61	0.41	0.17
propane	0.12	0.13	0.03
ΣC_4	0.08	0.11	0.03
CO	26.84	32.69	41.60
CO ₂	56.25	54.14	49.50
H ₂	6.56	4.34	2.71

Table 6 Composition of gas from fast pyrolysis of waste PET at different final temperatures

	360 $^{\circ}\text{C}$	380 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$
methane	3.18	1.98	2.08
ethylene	5.80	5.72	4.38
ethane	0.21	0.13	0.10
propylene	0.32	0.34	0.18
propane	0.21	0.05	0.06
ΣC_4	0.08	0.09	0.04
CO	31.88	37.18	42.80
CO ₂	53.69	50.80	47.54
H ₂	4.63	3.71	2.82

Table 7 Comparison of total gas compositions at final temperatures of 360, 380 and 400 $^{\circ}\text{C}$. w – heating rate ($^{\circ}\text{C/min}$)

w	Components	360 $^{\circ}\text{C}$	380 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$
5	CO + CO ₂	83.09	86.83	91.10
	C ₁₋₄	10.35	8.83	6.19
	H ₂	6.56	4.34	2.71
25	CO + CO ₂	85.57	87.98	90.34
	C ₁₋₄	9.80	8.31	6.84
	H ₂	4.63	3.71	2.82

As mentioned above, the losses were acceptable (Table 1) but not negligible. It is therefore necessary to find their cause. With slow pyrolysis, the losses increased with increasing gas and liquids production, on the other side, in the case of fast pyrolysis the lowest losses, almost zero, at the highest gas and liquids yields were recorded. Further, losses in slow pyrolysis (6–8%) were higher than those in fast one (0–5%). These phenomena can be explained on the basis of experience with the pyrolysis unit

used [25] and the decomposition behavior of plastics. As we found, the cause of the losses was not the leakage of gas/volatile substances only, but also the deposits on the glass tubes transporting the raw gas. FTIR analysis of these deposits showed that mainly quinones and esters were deposited. Quinones and esters were also identified in the FTIR spectra of the liquid fractions obtained at both heating rates at the considered final temperatures. For slow pyrolysis it is demonstrated in Fig. 4.

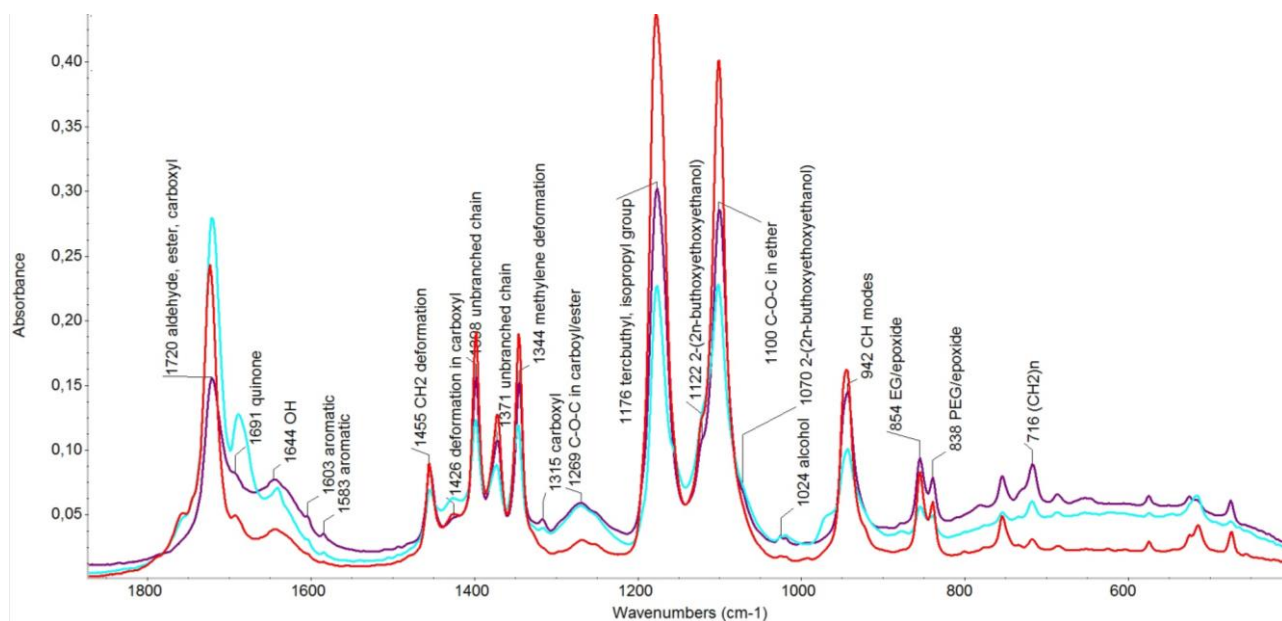


Fig. 4 FTIR spectra of the liquid fractions in the range of 1800–500 cm^{-1} . (Slow pyrolysis, final temperatures: 360 °C – turquoise line, 380 °C – red line, 400 °C – purple line). Identification (cm^{-1}): 1720 – aldehyde, ester, carboxyl; 1691 – quinone; 1644 – OH in water; 1603, 1583 – aromatics; 1455, 1344 – CH_2 ; 1426, 1315 – carboxyl; 1398, 1371, 716 – CH_2 in unbranched chains; 1269 – ester; 1176 – isopropyl in paraldehyde; 1100 – C-O-C in paraldehyde; 942 – CH; 854, 838 – ethylene glycol

Since viscosity is an important parameter from a practical point of view, the dynamic and kinematic viscosity of the obtained oil was determined and compared with those of ethylene glycol standard and commercial antifreeze mixtures of the Fridex type (Table 8). The table shows that the viscosity of the oil obtained is comparable to that of the Fridex G 48 mixture.

4. Conclusions

The thermal degradation of waste PET under low-temperature conditions was studied. Both slow and fast pyrolysis were tested. In both cases, it was found that at the final temperature of 400 °C, products with high utility value are formed, namely the solid fuel with HHV 31–32 MJ kg^{-1} and LHV 30–31 MJ kg^{-1} , ethylene glycol and/or aldehydes as useful chemicals. Quinones in decomposition products have also been newly discovered. However, it must be said that the conditions for the formation of ethylene glycol and its further evidence have yet to be investigated.

Table 8 Viscosity of oil from PET at 20 and 40 °C (pyrolysis at 25 °C min^{-1} , final temperature 400 °C) and comparative liquids (measurement with a Thermo Scientific Haake viscotester iQ)

Liquid	°C	Dynamic viscosity (mPa s)	Kinematic viscosity ($\text{mm}^2 \text{s}^{-1}$)	Density at 20 °C (kg m^{-3})
Oil obtained	20	10.87 ± 1.08	10.1	1080
	40	8.65 ± 0.02	-	-
Fridex Stabil	20	22.22 ± 1.85	19.7	1130
	40	12.55 ± 0.43	-	-
Fridex G 48	20	7.80 ± 0.59	6.9	1125
	40	5.64 ± 0.02	-	-
Ethylene glycol	20	21.06 ± 0.35	18.9	1114
	40	12.37 ± 0.19	-	-

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List of abbreviations

PET – polyethylene terephthalate
 EG – ethylene glycol
 TCD – thermal conductivity detector
 FID – flame ionization detector
 HHV – higher heating value
 LHV – lower heating value
 FC – fixed carbon
 VM – volatile matter
 GC-MS – gas chromatography mass spectrometry
 ATR – attenuated total reflectance method

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