The influence of process parameters on combustion of plastic waste in the fluidized bed reactor

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The paper presents the results of a research on the effects of process parameters on the combustion of waste plastics. The experiments were carried out in a laboratory fluidized bed reactor. The temperature and the conditions of the process were changed during the experiments. The plastics were combusted continuously (autothermally), periodically with extra fuel (co-firing) and alone in a hot fluidized bed. During the combustion process of materials containing nitrogen (PA, ABS), while the bed temperature decrease, changes of emissions of nitrogen oxides, in particular an increase in the concentration of N_2O, up to 250 ppm at ~730ºC, were observed. During ABS combustion, emission of HCN was registered, at a maximum of 400 ppm. The presence of the supporting fuel (LPG) resulted in the stabilization and acceleration of the plastic samples degradation process. The rate of thermal decomposition of waste materials depended on its elemental composition and also the physicochemical properties.

Keywords: plastics, fluidization, combustion, thermal decomposition, polymers, fluidized bed reactor, municipal waste, waste utilization, fluidized bed.

INTRODUCTION

In recent years the production of plastics in the world has increased significantly. In the year 2011 approximately 280 million tons of polymer-based materials were produced, including approximately 58 million tons in Europe. Synthetic materials are used in almost every industry sector. The largest demand for plastics, consistently over the years, is observed in the manufacturers of packaging industries and construction[1].

In Europe many initiatives to completely eliminate the problem of waste plastic storage in landfills were undertaken. In some countries, like Sweden or Germany, the level of recovery of plastics from municipal waste has reached 90%. In many countries, the level of recycling is still too small. In the year 2011 in Poland 157.3 thousand tons of plastic waste were selectively collected. It is definitely more than in previous years, but only 1.6% of the total weight of municipal waste collected in 2011[1–2].

For industrialized countries, the share of plastics fraction in the municipal waste shall be adopted in the range of 2–10%. In 2001–2005 in Poland, 12–18% of the total weight of waste was a fraction of plastics. Together with the country's economic development and social environmental awareness, the share of recyclable materials going to landfill decreased from year to year[3–4].

The thermal treatment of municipal waste by the combustion process is one of the possibilities of its utilization. Differentiation of the quality of this waste makes the process of combustion complex. The waste incineration plant, in addition to emissions of pollution typical of combusting conventional fuels (CO, CO_2, NO_x, SO_2 and dust), emitted also more dangerous compounds such as polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDF), heavy metals and chlorinated biphenyls (PCD)[5–6].

In Europe, the major emphasis is on avoiding, reducing, and above all preventing emission of pollutants into the environment in every sphere of life. The degree of thermal conversion of waste and the accompanying emissions of harmful substances, is a result of not only the quality of the combusted material, but also the conditions under which the process is carried out. EU law strictly defines the requirements to be met by municipal waste incinerators. European Directives regulate the levels of pollutants released into the environment and the process conditions, which have to be met by waste incineration plants[7–12].

EXPERIMENTAL PART

In the studies samples of popular plastics, which came from municipal or production waste, were used. The

Table 1. Composition of the flue gases from combustion of plastics

| Plastic samples	LDPE	PP$_{type1}$	PA	PET	PC$_{type1}$	ABS	PP$_{type2}$	HDPE	PC$_{type2}$	PS
T$_{50}$, ºC	885	847	746	860	880	83	799	789	863	805
O$_2$, %	6.3	7.0	11.5	8.6	7.2	8.3	9.1	8.7	9.2	6.7
CO, ppm	2701	3218	354	1639	2303	2136	2062	2421	1354	4246
CO$_2$, %	9.5	9.4	6.3	11.1	10.7	9.1	8.3	8.9	10.1	10.9
NO$_x$, ppm	29	55	787	13	46	585	23	25	107	70
N$_2$O, ppm	0	0	175	0	0	55	0	0	0	0
HCN, ppm	30	48	57	11	19	165	22	19	9	90
VOC, mg/dm^3	661	2365	197	925	1178	1043	1363	2194	329	1603
Methane, ppm	1558	1762	952	1275	1362	1320	1439	1417	1098	1829
Ethene, ppm	297	292	9	25	39	79	138	199	22	186
Phenylethene, ppm	0.0	0.0	0.0	0.0	0.0	15	0.0	0.0	0.0	54

plastics which came from municipal waste were identified by index 'h' (household waste) e.g. PET_h. The materials were divided into packaging, which include: LDPE, PP, PET, PC, HDPE, PS and construction: ABS, PA and PVC. The samples used in the studies were in the form of pellets, regrinds and the pellets from plastics waste with an average size of 6 mm. In the case of household waste the samples were rectangular in shape with an average size of 15 x 20 mm. The elemental composition of the selected plastics was shown in the Table 4.

The experimental tests were conducted in the laboratory fluidized bed reactor, previously used for solids or gaseous fuels combustion[13–20]. The experiments were carried out in a laboratory fluidized bed reactor with a thermal power of about 5 kW. The reaction chamber was built with a quartz glass cylinder of 500 mm height and an internal diameter of 96 mm. Quartz sand of 0.385–0.43 mm particles diameter and weighing approx. 400 g was used as the bed material. A schematic representation of fluidized bed reactor was shown in the Figure 1.

Tests were conducted in three types of operation, under the variable conditions of the combustion process. In the first variant, the experiments took place under the autothermal conditions. Heating of the fluidized bed took place with the supporting, gaseous fuel (LPG). While the fluidized bed temperature reached about 950°C, LPG was closed and the reactor was supplied only by plastics fraction. Next, different types of materials were introduced into the reactor using an automatic dispenser.

In the second variant of the tests, the process of co--combustion was used. Single samples of plastics were applied into the working fluidized bed at appropriate time intervals. The reactor was powered by gaseous fuel during the experiments, which allowed to maintain a stable bed temperature in the range 850–950°C.

In the last phase of the research, the separated particles of plastics were combusted without the assisting extra fuel. When the temperature of the fluidized bed reached the desired range around 900°C and flue gas composition was stable, then gas supply was closed and the solid sample was dosed into the bed. When the examined material was combusted in the bed, the bed
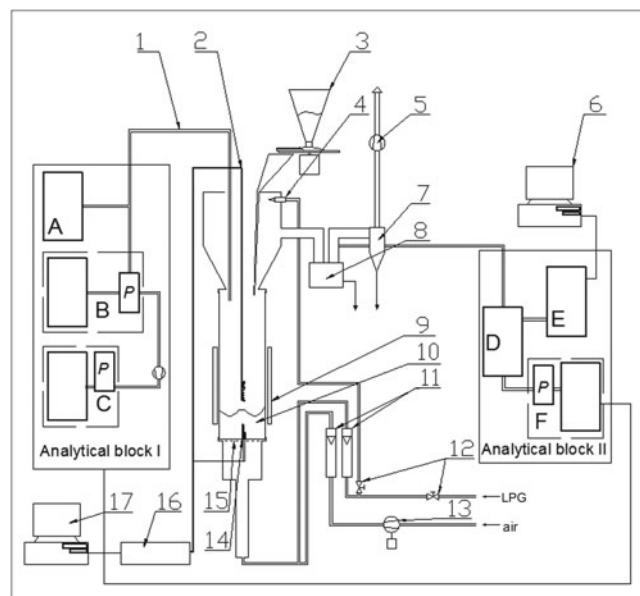
1 – heated probe for flue gases sampling, 2 – set of thermocouples, 3 – feeder of plastic samples, 4 – pilot flame, 5 – exhaust fan, 6 – computer for Gasmet DX-4000 analyzer, 7 – cyclone, 8 – ash trap for coarser particles, 9 – movable radiation shield, 10 – bubbling fluidized bed, 11 – rotameters (air and primary fuel), 12 – fuel supply valves (for pilot flame and reactor), 13 – fluidizing air blower, 14 – two thermocouples, 15 – flat, perforated metal plate distributor, 16 – A/D convertor for thermocouple signals, 17 – computer storing chemical analyses quantities and temperature, A – total organic compounds analyser (JUM Model 3-200), B – O_2, CO, NO, NO_2, SO_2 analyser (ECOM SG Plus), C – CO_2 analyser (Madur), D – N_2O analyser (Horiba VA3000), E – O_2, CO, CO_2, SO_2, NOx, N_2O analyser (Horiba PG250), P – Peltier's cooler, F – mobile conditioning system of Gasmet DX-4000 analyzer, G – FTIR analyzer (Gasmet DX-4000), H – O_2, CO, NO, NO_2, SO_2, CH_4, CO_2 analyzer (MRU Vario Plus).

Figure 1. Schematic representation of fluidised bed reactor

layer was fluidizing only by the heated air stream fed from the bottom of the reactor. Analytical equipment used during the study, was divided into two separate blocks. The first analytical block consisted of the measuring equipment such as Total Hydrocarbon Analyzer 3-200 (J.U.M. Engineering GmbH), ecom-SG Plus, rbr Messtechnik GmbH Company (O_2, CO, NO, NO_2, SO_2), PG250, Horiba Company (NO_x, O_2, CO, CO_2 and SO_2). To analyze the composition of the diluted exhaust gas, a second measuring block, was also used. This block

Table 2. Visualization of the process of co-combustion and self-combustion of the particles of polyamide (PA) in a bubbling fluidized bed

Co-combustion PA with LPG	Self-combustion PA without LPG
Mass sample: 0.564 g	Mass sample: 0.741 g

Table 3. Average times of co-combustion with LPG and total combustion time without LPG of selected samples of plastics

Co-combustion with LPG				Self-combustion without LPG		
Plastics	Mass, g	Average time, s		Plastics	Mass, g	Total time, s
		CO_2	LZO			
PET_h	0.549	10.2	7.2	PET_h	0.567	16.8
$PEHD_h$	0.625	9.8	7.1	$PEHD_h$	0.314	9.0
ABS	0.403	12.9	11.0	ABS	0.411	29.8
PA	0.313	20.6	9.6	PA	0.741	33.5
PVC_h	0.545	13.9	12.0	PVC_h	0.412	42.6

consisted of the following apparatus: Vario Plus by MRU GmbH (O_2, CO, CO_2, NO, NO_2, SO_2 and CH_4) and DX-4000 Gasmet (which allows a simultaneous analysis of a number of inorganic and organic substances).

The identification and measurement of concentration in the exhaust gases were based on electrochemical, chemiluminescent, infrared absorption (nondispersive), flame ionization detection methods and the infrared spectroscopy with Michelson interferometer connected with Fourier transformation. This measurement was conducted online. In the studies on the dynamics of the thermal decomposition of plastics digital video recording, which was used for a detailed analysis of the phenomena occurring in the reaction chamber, was extremely helpful. During the experiment, the first camera used the speed of 25 frames/s and the resolution of 1088 × 1440 pixels (continuous recording) and the second camera with the recording speed of 250 frames/s and the resolution of 336 × 448 pixels (ten second recording).

DISCUSSION AND RESULTS

In Figure 2 the changes of temperature, concentration nitrogen oxides and hydrogen cyanide in the exhaust gases for various materials were shown. The temperature indicated on the graph (T_{50}) was measured at the height of 50 mm from the distributor. The stationary height of the bed was 45 mm, and the measured dynamic height was about 130 mm. The combustion process was conducted under autothermal conditions. The graph shows the effect of temperature on the increase of N_2O concentration during the combustion PA. In addition, combustion of nitrogen-containing materials (in the structure of the monomer), lead to increased emissions of NO_x in exhaust gases, for example in case PA. Elemental analysis for PA and ABS confirmed the presence of bound nitrogen. In the case of PPtype1, PCtype1 and PCtype2 the presence of nitrogen was not confirmed. The presence of nitrogen oxides in the flue gases during the combustion of the non N-fuel plastics, may be explained on the basis of the known "prompt" reaction of molecular nitrogen with hydrocarbon radicals.

In Table 1 the average values of the concentrations of selected inorganic and organic substances in the exhaust gas, measured during the combustion of different plastics in a continuous manner, were shown. Sulfur dioxide was not found in the flue gas. Nitrogen oxides NO and NO_2 were recognized as NO_x. The concentrations of the organic compounds in different sub-periods, were measured for such compounds for which the residual spectrum contains the fewest number of interferences. In Table 1 also the total concentration of VOCs, which was detected by the FID method, was shown. The calculations were performed for all sub-periods taking into account only the pure fraction of the plastic.

Selected images from the digital recording process of co-combustion and self-combustion of polyamide particles with different masses were shown in Table 2. As can be seen in the case of self-combustion PA, the excess oxygen in the particle surroundings allows an immediate oxidation of emerging gases. While the co-combustion process provides a constant temperature of the bed, so the combustion is more stable. During the processes of continuous combustion for either plastics or LPG, the air excess coefficient was 1.4. During the non-supported
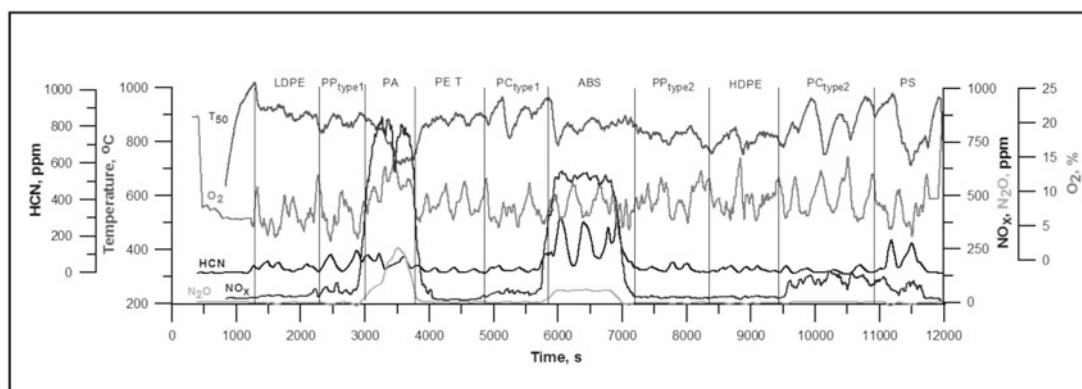

Figure 2. The changes of temperature and emission concentration of inorganic compounds as a function of time
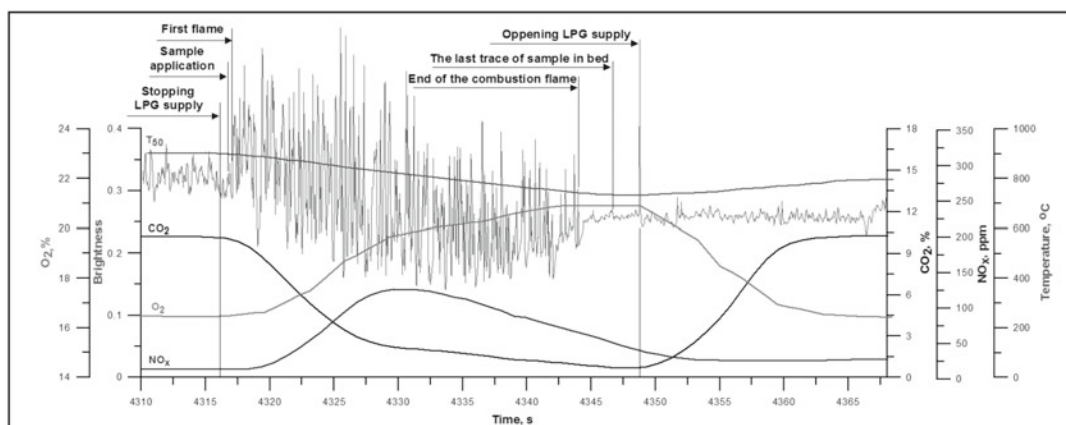

Figure 3. Dynamics of lighting effects accompanying the self-combustion of ABS (0.411 g) particle and temperature, concentration CO_2 and NO_x in exhaust gases as a functions of time

periodical combustion of the tested samples the fluidized air flow was not changed after switching off the supply of LPG. In the latter case, the O_2 excess in the reaction zone allowed the post-combust gases from the decomposed material.

Only in the case of the PA sample a clear residue after combustion was observed. This plastic had a body-filler in the form of fiberglass which, after the combustion process has retained its original shape. The residue after burning of the samples of PA was shown in Table5. This pictures shows the preserved skeleton structure of the tested samples. The residue of plastic had an unchanged shape under high temperature and work of the bed. Elemental analysis of PA revealed, that the non-combustible part of this material was about 31.6%. Other materials were almost completely combusted.

In previous articles other authors have attempted to determine the time of combustion of various plastic samples, which was based on the changes in the concentration of CO_2 and CO in the flue gases[21]. In our study, analysis of the dynamics of combustion plastic was carried out also on the basis of a sequence of the digital images. The mathematical interpretation of these images allows for more accurate determination of time of combustion of the sample in comparison with the data of the exhaust gas analyzers. In Fig. 3 changes in brightness, temperature and concentrations of carbon dioxide and nitrogen oxides during the combustion of plastic sample of the copolymer acrylonitrile-butadiene--styrene (ABS) with a weight of 0.411 g were shown. The process was conducted in the preheated bed to about 900°C. Observations prove the characteristic changes in the conditions of the combustion process, as marked and labeled in Fig. 3. The diagram shows the decrease in the intensity of light effects during combustion of the ABS

sample. The average time interval between successive ignitions of emerging gases during the combustion of ABS sample was about 0.53 seconds. A non-continuous (bubbled) mode of the flow of the gas phase through the fluidized bed affects the flame fluctuations, but it is not decisive. On the basis of our other studies under the same conditions, where biomass in the form pellets was combusted it was found that the average time between successive ignitions of gaseous products in the bed or on its surface was about 0.9 seconds[22]. On this basis, it can be assumed that the instability of the flames and the time interval between the ignitions depends on the type of the burned material and the rate of its pyrolysis, and not only on the nature of the fluidized bed. Various intervals of ignitions and gas explosions may indicate differences between the rates of release of combustible gases from the test material.

In Table 3 the time of co-combustion and self-combustion (without gas LPG) of selected plastics was shown. In the first case this time was determined on the basis of changes in the concentration of CO_2 and VOC emissions in the flue gas. However, the total time of self-combustion of plastics was determined on the basis of the digital video recording during the study. In the co-combustion process, due to a lack of regular lighting effects in the area above the bed, it was impossible to calculate the combustion times based on the charts of fluctuations brightness.

CONCLUSIONS

Under the conditions of the autothermal combustion process, the effect of temperature on the reduction of the concentration of nitrogen oxides in exhaust gases was observed. Particularly interesting results during the

Table 4. The elemental composition of the polymers

Plastics		PE LD	PP_{type1}	PA	PET	PC_{type1}	ABS	PP_{type2}	PE HD	PC_{type2}	PVC_h
Mass shares, %	C	85.1	82.2	44.1	61.7	76.1	63.6	85.5	85.5	75.6	28.8
	H	14.5	13.8	6.9	4.3	6.3	6.6	14.3	14.2	5.7	2.3
	O^1	–	–	41.4^2	34.0	17.7	–	–	–	18.6	
	N	–	–	7.6	–	–	2.9	–	0.2	–	–

[1] calculated from the results of the CHN;
[2] including approximately 31.6% of the non-combustible parts.

Table 5. Photos and mass of the PA before combustion and residues in the bed after it burned

Sample	Before combustion	After combustion	Mass, g	Residue mass, g	The share of non-combustible part, %
1			0.090	0.037	41.1
2			0.313	0.157	50.2
3			0.564	0.169	30.0
4*			0.741	0.163	22.0

*sample burned without extra fuel.

combustion of the PA and ABS materials, (containing nitrogen in the elemental composition) were obtained. In the case of polyamide, with increasing the bed temperature, a significant decrease of nitric oxide I (N_2O) was recorded (Fig. 2). However, in the case of combustion ABS, N_2O concentration was maintained at a constant level with little dependence on the fluidized bed temperature. In the exhaust gas the increased concentration of HCN was also observed.

Additional, supporting gaseous fuel have a distinct impact on the stabilization of the combustion process. The particles of plastic were evenly burnt during the time while heated by the fluidized bed. In the case of the hot fluidized bed, which was fluidizing only by air (without LPG), the excess oxygen in the reaction environment allowed immediate combustion of gases resulting from the decomposition of plastic material (Table 2).

Differences of the conditions of co-combustion process with LPG and self-combustion plastics in a hot fluidized bed, had a direct impact on the rate of degradation of the tested materials. Additional fuel allowed to maintain a constant bed temperature, in the results of that, the time of plastics co-combustion was shorter in comparison to the time of their self-combustion. On the rate of combustion, regardless of the presence of additional fuel, the impact had also a nature of plastics. The samples from packaging material were underwent to rapid thermal decomposition in bed than the samples from construction materials such as ABS, PA and PVC (Table 3). During the self-combustion of a sample in the hot fluidized bed, it was possible to observe and determine the successive stages of its thermal decomposition. The first flames after application of the sample into the bed, occurred after the time of induction, when the particle was heated. While, at the end, after the longest stage of the flame combustion the flameless combustion period began, which lasted until the sample can be evidently observed and localized in the bed (Fig. 3). These observations can be useful during the projection stage of thermal incinerator based on fluidization principle.

ACKNOWLEDGEMENTS

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