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# POLYCARBONATE COMBUSTION
# IN A FLUIDISED BED REACTOR

## SPALANIE POLIWĘGLANU W REAKTORZE FLUIDYZACYJNYM

**Abstract:** In the article there is some results of the realized experiments of some polycarbonate combustion in the laboratory fluidised bed reactor. The thermal utilization processes enable the total removal of the waste plastics from the environment with simultaneously the useable energy recovery possibility. The chemical composition of polycarbonate makes the thermal decomposition processes very difficult. The thermal decomposition of polycarbonate, as the high oxygen index plastic, requires some specific conditions of the process operation in order to the complete oxidation realization and the prevention of the emissions of some toxic substances into the atmosphere. The turbulence, the oxygen presence in the reaction zone and the high temperature of the fluidised bed ensure the favourable conditions of the thermal decomposition process in fluidised bed reactors. The combustion processes of this waste plastic may be a useable alternative energy source. The aim of the realized experiments is the examination of the polycarbonate combustion process parameters in fluidised bed reactors and the elaboration of the principal technological conditions of the thermal decomposition process.

**Keywords:** polycarbonate combustion, thermal decomposition, fluidised bed reactor

Polycarbonate is a synthetic thermoplastic polymer that is mainly produced by the polycondensation of bisphenol A with phosgene. Polycarbonate physical properties (transparency, mechanical strength and dielectric properties) make wide applications possible. It is used as an engineering plastic and probably the most meaningful parts of its production are for electrical and electronic industry (sockets, plugs, connectors, loudspeakers, electrical insulations, lamp enclosures, mobile phone enclosures), and also medical instruments (blood oxygenators, dialysis machines, optical glasses and diverse kinds of lenses) and automotive industry (automotive windows and lights, motorcycle windshield visors and helmets, streetlights, traffic signals). It is commonly used in lots of laboratory equipment (flash-light instruments, microscope parts, tubes, rods) and domestic utensils (electrical kettles, coffee makers, electrical grills, microwave ovens and other kitchen dishes and some package containers and also electric shavers, hair-dryers, tanks for flat irons) and some specific data carriers (identity cards, credit cards, compact discs and digital versatile discs). The polycarbonate, like most organic synthetic polymers, is built from carbon, hydrogen and oxygen atoms (the mass fraction of C : H : O = 0.756 : 0.055 : 0.189) and the average molecular weight of one macromolecule in the polymer structure can be equal form 25 000 to 75 000 and even 100 000. Polycarbonate is an amorphous polymer but partial crystalline forms can be also manufactured. The polymer melts when heated to 230ºC and when the temperature is above 320ºC it begins to decompose and the most efficient destruction process occur when the temperature is about 550ºC. The energy from the broken chemical bonds is released [1-6]. Bisphenol A polycarbonate presents good

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resistance to burning even without flame-retardant additives, it has an oxygen index (OI) of 26 and is listed as V-2 by Underwriters' Laboratory [7]. All the substances that are used to the considered polymer production (phosgene, bisphenol A - a condensation product of acetone and phenol) are not neutral to human health, so if the polycarbonate decomposition is possible, the waste polycarbonate wares should be properly utilized.

Combustion is a process of a high temperature oxidation. During this process the chemical compounds are destroyed with some new substances creation. The basic products of the complete combustion of the chemical compounds that are built from carbon, hydrogen and oxygen atoms are carbon dioxide and water vapour [8]. In fact any kind of combustion is a very complicated process with a sequence of intermediate steps and not always the complete combustion products are created in the first combustion zone. The most harmful incomplete combustion products, mainly including carbon monoxide and volatile organic compounds, have to be oxidized in the next combustion zone, what is practically applied in industrial combustion plants and waste incinerators [9].

Fluidised bed reactors are very favourable devices for thermal utilization of diverse kinds of waste [10, 11]. In industrial fluidised bed reactors the chemically inert or active bed is fluidised by some air and the combustible substances are mixed with the fluidised bed and with the air which is the oxygen source. When the considered burned substances are relatively resistant to decomposing, and thus difficult to oxidizing, then the hot fluidised bed particles heat these substances up and facilitate and accelerate their thermal decomposition.

Concerning all the previous mentioned facts, the utilization of waste polycarbonate wares in fluidised bed reactors was proposed as the applicable method of the thermal disposal of this plastic from the environment. Plastics are very common solid municipal waste components. Their wide applications contribute to the presence of them in almost all kinds of waste. Nowadays a great deal of waste is burned in industrial incineration plants as a result of the obligatory policy [9] and the special care have to be imposed to the prevention of the emissions of some toxic substances into the atmosphere. The benefits will enclose the whole environment.

**Experimental data and discussion**

The experiments of the thermal decomposition of some bisphenol A polycarbonate, which chemical structure is in Figures 1 and 6, were carried out in the laboratory bubbling fluidised bed reactor - schematically presented in the Figure 2. The experiments were realized as the combustion process of some polycarbonate samples with propane, a high calorific saturated aliphatic hydrocarbon that was used to the maintenance of the appropriate temperature conditions.

The whole laboratory site consisted of the fluidised bed reactor itself and the accompanying operating, controlling and measuring devices. The reactor was the vertical oriented cylindrical quartz tube of the height 500 mm and the diameter 96 mm and it rested on the flat perforated Cr/Ni steel distributor. The total amount of the circular holes in the distributor was equal to about 450 and their diameters were equal to 0.6 mm. The air and the propane were supplied to the reactor plenum chamber by the separate pipes with each gas flux controlling, the stream of air was equal to 1.650 $dm^3$/s and the stream of propane was equal to 0.046 $dm^3$/s resulting in the 50% of the air excess.
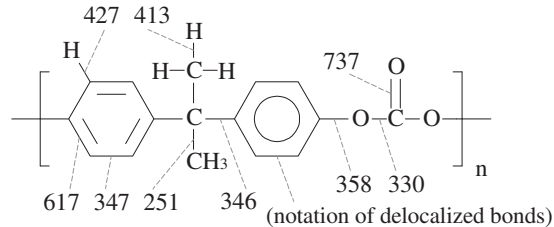
427 413

737

(notation of delocalized bonds)

617 347 251 346 358 330

Fig. 1. The bisphenol A polycarbonate bond dissociation energies [kJ/mol] [4]

1 - plenum chamber
2 - bubbling fluidised bed
3 - freeboard space
4 - perforated distributor
5 - reactor cover
6 - pilot flame
7 - bed thermocouples
8 - insulating shield
9 - air blower
10 - air blower controller
11 - air rotameter
12 - air pipe
13 - propane container
14 - propane rotameter
15 - propane pipe
16 - flue gas probe
17 - ash trap
18 - cyclone
19 - exhaust fan
20 - valve
21 - analytical block
     with flue gas analysers
     Horiba PG-250
     Horiba VA-3000
     MRU Vario Plus
     Ecom SG Puls
     J.U.M. 3-200
22 - A/D converter
23 - digital camera
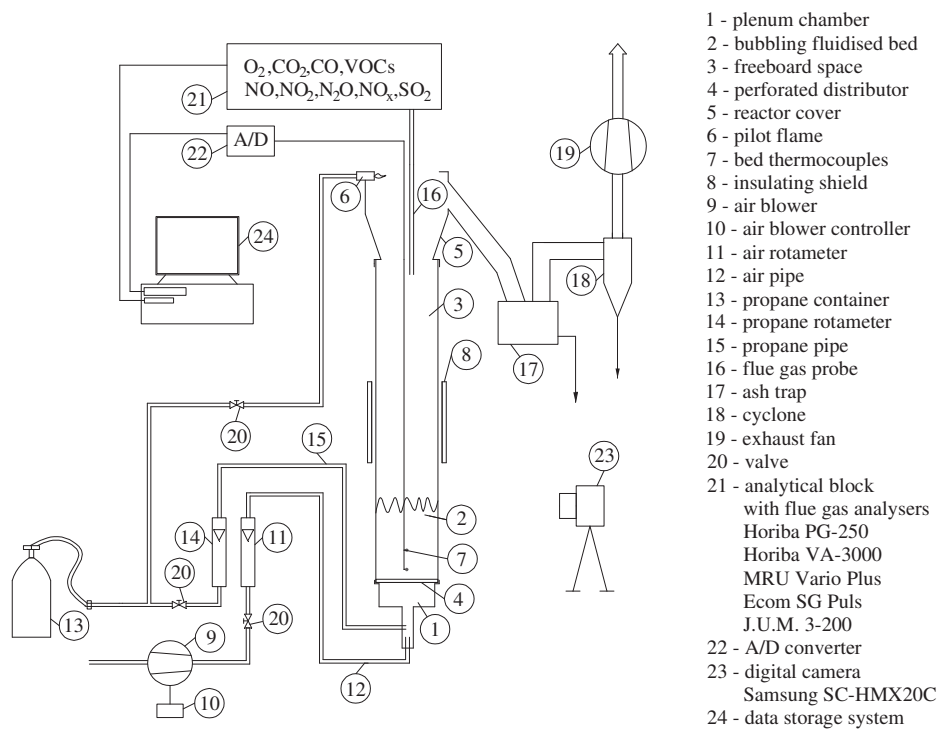     Samsung SC-HMX20C
24 - data storage system

Fig. 2. The scheme of the laboratory fluidised bed reactor

The hydrocarbon fuel was burned in the reactor bed and the exothermic combustion reactions heated the fluidised sand bed up. The total mass of the quartz sand particles was equal to 300 g and the diameters of the sand particles were about from 0.385 to 0.430 mm. While the realization of the main stages of the experiments, the temperature of the sand bed measured by two Cr/Ni-Ni thermocouples located 20 and 50 mm above the distributor was equal to 900ºC or even 960ºC when the insulating shield covered a part of the reactor tube. The exhaust pipe was localized at the top of the reactor and the flue gases were transported through the ash trap and the cyclone and were taken out from the reactor by the operation of the exhaust fan which released them into the atmosphere. The concentrations of the selected

components in the flue gases were monitored by using special technically available methods and the digital camera was used to take some photos (Figs 3-5).



Fig. 3.  The fluidised bed reactor just after the ignition of propane–air mixture (bed temperature 400ºC)
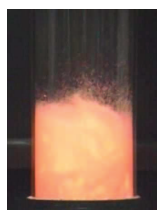


Fig. 4.  The fluidised bed combustion of propane (bed temperature 900ºC)



Fig. 5.  The fluidised bed combustion of propane with some polycarbonate sample (bed temperature 900ºC)

The analytical block of the laboratory site included four gas analyser devices that applied different analytical methods:
-   Ecom SG Plus gas analyser: $O_2$, CO, NO, $NO_2$, $SO_2$ (electrochemical method)
-   MRU Vario Plus gas analyser: $O_2$, CO, NO, $NO_2$, $SO_2$ (electrochemical method), $CO_2$ and the sum of volatile organic compounds (infrared radiation method)
-   Horiba VA-3000 and PG-250 gas analysers: $CO_2$, CO, $N_2O$, $SO_2$ (infrared radiation method), $O_2$ (electrochemical method), NO, $NO_x$ (chemiluminescent acid method)
-   J.U.M. 3-200 gas analyser: total volatile organic compounds (flame ionization detector method)
and Samsung SC-HMX20C digital camera enabled to take 250 pictures per second (336 pixels x 448 pixels).

It was observed that while the thermal decomposition of some polycarbonate samples in the fluidised bed reactor, as contrasted with only propane combustion, some flames were present. The flames appeared in the bed and they came to the reactor freeboard space where they vanished gradually. The careful observations allowed to state that the whole process started in the hot fluidised sand bed where the vapour bubbles around each polycarbonate

particle were created. The vapour bubbles were supposed to consist of the polycarbonate pyrolysis products.
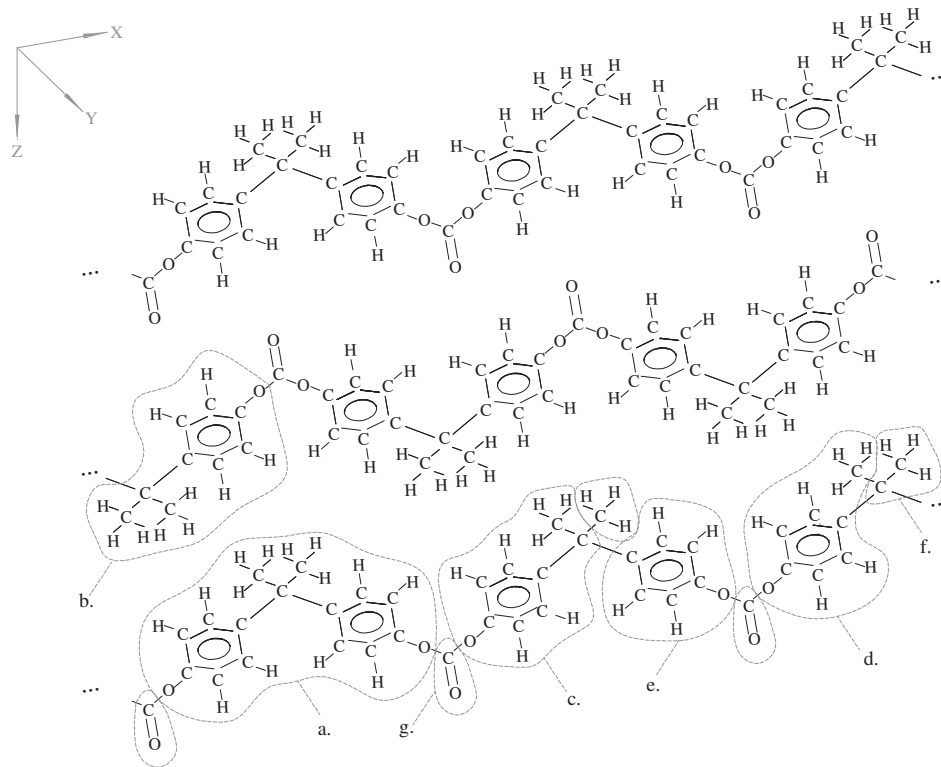


Fig. 6. The polycarbonate structure and the suggested scheme of the formation of some polycarbonate pyrolysis products: a) bisphenol, b) 4-propylphenol, c) 4-ethylphenol, d) 4-methylphenol, e) phenol, f) hydrocarbon, g) carbon monoxide, in a) to e) 'sub-pictures' the broken bonds need some hydrogen atoms for the suggested chemical compounds formation, the hydrogen atoms are present in f) and the rested carbon atoms from f) could be easily oxidized in combustion processes, the chemically bonded carbon atoms could also create some polycyclic carbon structures

The suggested scheme of the formation of some polycarbonate pyrolysis products is schematically presented in Figure 6. During the pyrolysis process the chemical bonds are usually broken in the sequence form the lowest to the highest bond dissociation energies. It was notices that after the diameters of the bubbles in the bed achieved about 20 mm, the pyrolysis products started to come from the fluidised bed, so some specific volume of the pyrolysis products was needed before these substances could be ignited by the surrounded combustible propane - air mixture and then could be oxidized. Probably the concentrations of the hydrocarbon radicals in the vapour bubbles were then sufficient to start the combustion process of the other pyrolysis products. The diffusion of oxygen to the pyrolysis products in the freeboard space contributed to the total disappearance of the
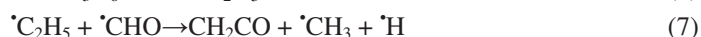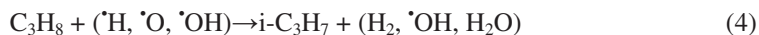
blazing flames before the exhaust gases entered into the flue gas probe. As a consequence nearly 100% of the carbon atoms that were built into the polymer structure turned into carbon dioxide molecules, the mass fractions of the monitored incomplete combustion products (CO and VOCs) in the flue gases were negligible. Despite this fact, the shining flames were the proof of the formation of some polycyclic aromatic hydrocarbons in the flue gases what contributed to the creation of some soot that covered the reactor quartz tube. The absence of some proper thermal insulation made a complete combustion process very difficult.

The combustion is a sequence of lots of radical reactions and the proceeds of them depend on the combustion process conditions, such as temperature, pressure and the kinds and the concentrations of the combustible mixture components. In case of polycarbonate with propane combustion the possible radical reactions include aliphatic hydrocarbon fuel oxidation processes and the reactions of the conversions and the destructions of the aromatic rings. There are many stages of the whole process and the great number of the reactions makes the precise studies very difficult. The crucial issue for the combustion processes of hydrocarbon fuels is the presence of such radicals as: $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}OH$ and $^{\bullet}CH_x$ in the gaseous reactivity zone. Some possible reactions during combustion of polycarbonate with propane are proposed below [8, 12]:

The radicals $^{\bullet}H$, $^{\bullet}O$, $^{\bullet}OH$ may be produced at high temperature by the destruction of the molecules while the collisions with the hot reactor walls:

$$^{\bullet}H + O_2 \rightarrow {}^{\bullet}O + {}^{\bullet}OH \tag{1}$$

$$^{\bullet}O + H_2 \rightarrow {}^{\bullet}H + {}^{\bullet}OH \tag{2}$$

$$^{\bullet}OH + H_2 \rightarrow {}^{\bullet}H + H_2O \tag{3}$$

The aliphatic hydrocarbon (propane) is decomposed by the abstraction of the hydrogen atoms and then the intermediate products are gradually oxidized:

$$C_3H_8 + ({}^{\bullet}H, {}^{\bullet}O, {}^{\bullet}OH) \rightarrow i\text{-}C_3H_7 + (H_2, {}^{\bullet}OH, H_2O) \tag{4}$$

$$i\text{-}C_3H_7 \rightarrow i\text{-}C_3H_6 + {}^{\bullet}H \tag{5}$$

$$C_3H_6 + {}^{\bullet}O \rightarrow {}^{\bullet}C_2H_5 + {}^{\bullet}CHO \tag{6}$$

$$^{\bullet}C_2H_5 + {}^{\bullet}CHO \rightarrow CH_2CO + {}^{\bullet}CH_3 + {}^{\bullet}H \tag{7}$$

$$CH_2CO + {}^{\bullet}O \rightarrow CH_2O + CO \tag{8}$$

$$^{\bullet}CH_3 + {}^{\bullet}O \rightarrow CH_2O + {}^{\bullet}H \tag{9}$$

$$CH_2O + {}^{\bullet}O \rightarrow {}^{\bullet}CHO + {}^{\bullet}OH \tag{10}$$

$$^{\bullet}CHO + {}^{\bullet}O \rightarrow CO + {}^{\bullet}OH \tag{11}$$

$$CO + {}^{\bullet}OH \rightarrow CO_2 + {}^{\bullet}H \tag{12}$$

While combustion of polycarbonate lots of phenoxy radicals are present because of the decomposition of the bisphenol groups. The process of the detachment of the methyl groups from the bisphenol groups proceeds easier than the destruction of the ring structures. The delocalized bonds make the 'rings' relatively thermally resistant.

In Figure 7 there is a sequence of the reactions during the phenoxy radical oxidation represented and in Figure 8 the mechanism of the polycyclic aromatic hydrocarbon growth

is illustrated. The presence of the ring structures in the reactionary combustion zone makes the greater possibility to some soot creation.
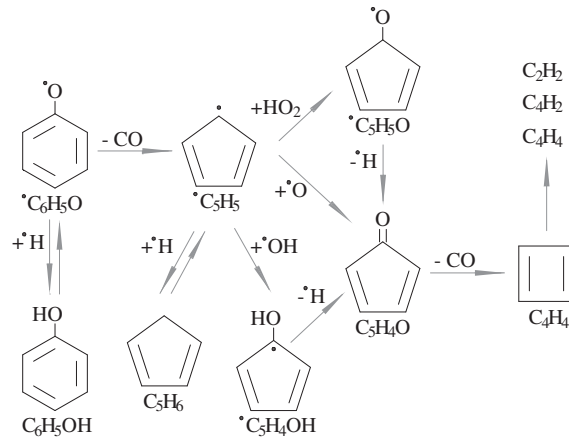


Fig. 7. The pathways of the reactions during the phenoxy radical oxidation [8]
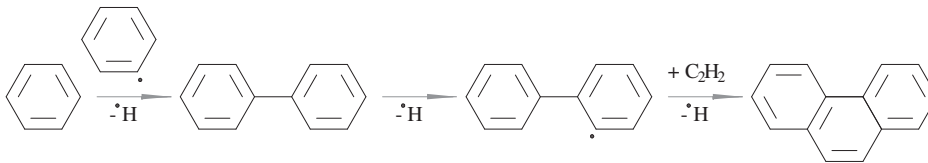


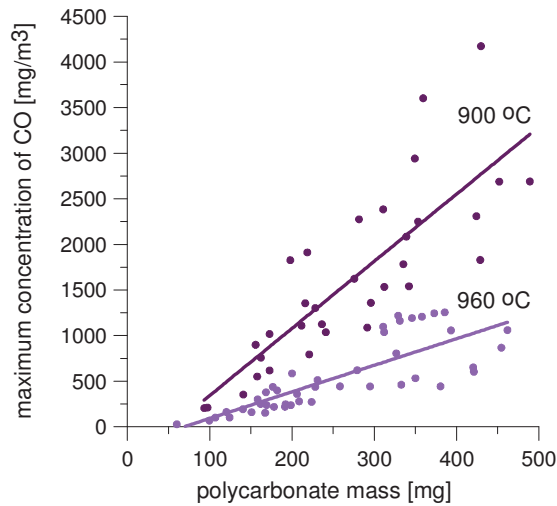Fig. 8. The mechanism of the polycyclic aromatic hydrocarbon growth [8]



Fig. 9. The maximum concentrations of the emitted carbon monoxide in the flue gases versus the masses of the burned polycarbonate samples in 960 and 900°C
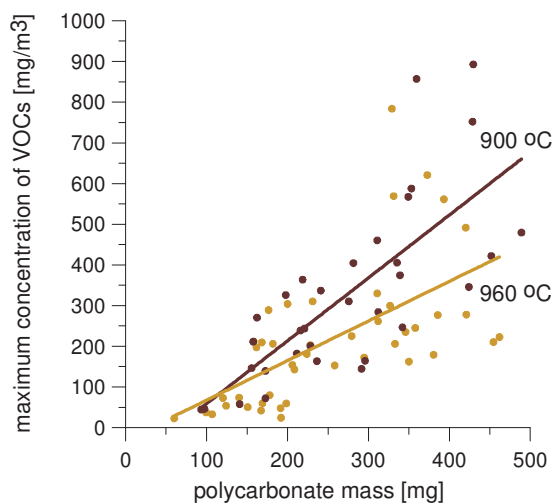
Fig. 10. The maximum concentrations of the emitted volatile organic compounds in the flue gases versus the masses of the burned polycarbonate samples in 960 and 900ºC
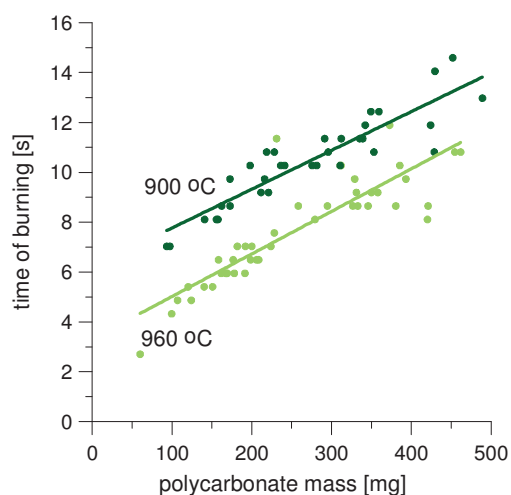


Fig. 11. The duration of the burning process of the polycarbonate samples in 960 and 900ºC (four particles in each sample)

The experiments that were carried out in the different temperature conditions and with the different quantity of the polycarbonate particles thrown into the hot fluidised sand bed simultaneously allowed to draw some conclusions. The higher temperature contributed to the better progress of the oxidation reactions and thus the lower emissions of the incomplete combustion products were observed then. While the thermal decomposition of some polycarbonate samples in the higher temperature conditions (960ºC), the maximum emission values of carbon monoxide and volatile organic compounds in the flue gases were lower, if comparing to these emission values in the lower temperature conditions (900ºC).

In the higher temperature conditions the thermal decomposition process of the analysed polymer proceeded quicker because the time of burning of the same polycarbonate mass was shorter. The thermal decomposition processes of all the polymer particles, that created one polycarbonate sample, proceeded independently and that is way the same time was needed for the greater total polycarbonate mass burning when the sample consisted of the greater numbers of the particles. In other words, when the polymer particle was smaller, resulting in smaller particle mass, then the whole burning process took shorter. All the mentioned facts were presented in Figures 9-12 and they arise from the combustion process kinetics.
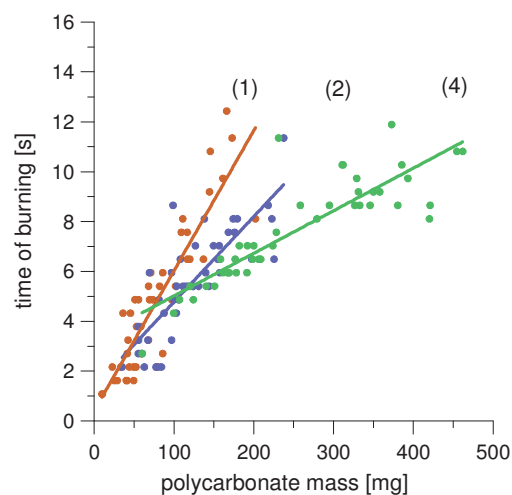


Fig. 12. The duration of the burning process of the polycarbonate samples consisted of the different quantities of the particles (bed temperature 960ºC)

The maximum values of the emissions of the incomplete combustion process products are important because when fuels or waste are burned in combustion plants or incineration plants, the values of the emissions that must not be exceeded are given in the obligatory laws as the maximum concentrations of some substances in the exhaust gases [13, 14]. The total amounts of carbon monoxide and volatile organic compounds depended on the process conditions and the mass of the burned polycarbonate but the concentrations of the pollutants in the flue gases are measured in industrial combustion plants or thermal waste utilization systems. The proper process conditions could ensure low emissions of harmful pollutants.

## Conclusions

In most aliphatic hydrocarbons the molar ratio of carbon atoms to hydrogen atoms is about a half what contributes to the specific combustion conditions with lots of radicals. In aromatic hydrocarbons there is often more carbon atoms than hydrogen atoms and the carbon atoms are bonded in ring structures which create the relatively strong chemical structures. These facts are meaningful when pyrolysis and oxidative reactions during combustion processes are considered. Polycarbonate, as a polymer with a lot of aromatic

bonds in its structure, is very resistant to thermal decomposition processes and it is also susceptible to forming some pollutants during thermal utilization [15]. The laboratory fluidised bed reactor with the continuous mixing of the burned substance with the air excess and some high calorific aliphatic hydrocarbon fuel in the atmosphere of the hot chemically inert material (quartz sand) ensured the specific conditions for the thermal decomposition processes.

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**Abstrakt:** Przedstawiono wyniki eksperymentów spalania poliwęglanu w laboratoryjnym reaktorze fluidyzacyjnym. Procesy termicznej utylizacji umożliwiają całkowite usunięcie odpadowych tworzyw sztucznych ze środowiska przy jednoczesnej możliwości odzysku energii. Budowa chemiczna poliwęglanu utrudnia prowadzenie procesów termicznego rozkładu. Rozkład termiczny poliwęglanu, jako tworzywa sztucznego o wysokim indeksie tlenowym, wymaga specyficznych warunków prowadzenia procesu w celu możliwości realizacji całkowitego utlenienia oraz uniknięcia emisji szkodliwych substancji do atmosfery. Turbulencja, obecność tlenu w strefie reakcji oraz wysoka temperatura fluidyzującego złoża zapewniają korzystne warunki prowadzenia procesu termicznego rozkładu w reaktorach fluidyzacyjnych. Procesy spalania odpadowych tworzyw sztucznych mogą stanowić użyteczne źródło alternatywnej energii. Celem realizowanych eksperymentów jest zbadanie parametrów spalania poliwęglanu w reaktorach fluidyzacyjnych oraz opracowanie zasadniczych technologicznych warunków procesu termicznego rozkładu.

**Słowa kluczowe:** spalanie poliwęglanu, termiczny rozkład, reaktor fluidyzacyjny