

EXPERIMENTAL STUDY OF WASTE RUBBER PYROLYSIS AND COMBUSTION

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Abstract

Experimental and theoretical investigation of combustion and pyrolysis of a single rubber particle is presented. Experiments were carried out in an equipment by applying the TGA and DTG methods. The pore structure of original and partially devolatilized particles was analysed. The particle was pyrolysed in a nitrogen flow and consecutively combusted at a wide range of initial temperatures and contents of oxygen in the inlet gas. The influence of temperature and concentration of oxygen on ignition temperature of rubber was also measured.

The results indicate that the rubber particle during thermal degradation released gradually volatiles, and the pyrolysis accounted for two significant stages. During the pyrolysis, an „opening“ of the rubber internal surface took place, and the value of porosity increased from 0% to more than 30%. The combustion time decreased with an increase in the initial temperature and the concentration of oxygen in the feed stream.

Key words: *combustion, pyrolysis, waste rubber, thermogravimetry*

The disposal of used automotive tyres has caused many environmental and economical problems to most countries. It is estimated that 2.5 million tons per year are generated in the European Union, 2.5 million tons annually in North America and around 1 million tons annually in Japan ^[1]. Most of the scrap tyres are dumped in open or landfill sites. For example, the Slovak Republic is producing 940.000 automobile tyres per year with an average growth of about 3% annually. Since 2002 waste tyres have been handled to rubber granulates, and then used as a substance for manufacturing sound insulation panels, pavement surfaces, railway crossings, microporous tubes or sport grounds.

Based on the information obtained from the Bureau of Statistics in the Slovak Republic the amount of motor-car and truck bald tyres represents annually 12 300 tons only in Slovakia. The scrap tyre is bulky and does not degrade in

landfills. Therefore, open dumping of scrap tyres occupies a large space, presents an eyesore, causes potential health and environmental hazards, but also illustrates wastage of valuable energy resource. It is well known that tyre is made of rubber materials (polybutadiene, styrene-butadiene rubber and polyisoprene or natural rubber), carbon black and some fibrous materials ^[1]. It has a high content of volatile compounds and fixed black carbon with a heating value higher than that of coal. This makes rubber from old tyres a good raw material for thermochemical processes. How to recover the energy from tyre is an acute and imperative problem for energy researchers ^[3]. The waste tyres can be used for:

- *recycling* and reuse of raw material
- *landfilling*
- *thermal treatment* – pyrolysis
– combustion
- *filling of construction materials*, etc.

In the pyrolysis process (heating without oxygen), the organic volatile matters of tyres (mainly the rubber polymers) are decomposed to low molecular weight products (liquids or gases), which can be used as fuels or raw materials for chemicals. The inorganic components (mainly steel) [2] and the non-volatile carbon black remain as solid residues relatively unaltered. Therefore, they can be recycled in useful applications [2].

In both pyrolysis and combustion, primary pyrolytic reactions take place, and therefore the study of their kinetics is interesting. Thermogravimetric analysis is one of the most used methods to study these primary reactions. In this work we investigated the possibility of the employment of a thermogravimetric equipment, constructed in our laboratory, for the pyrolysis and combustion of rubber. The experiments were carried out under different conditions (temperature and oxygen concentration). The pore structure of the pyrolysis solid products was also analysed.

This paper reveals two characteristic zones in the DTG curve of a rubber sample: in the first zone, decomposition of the processing oil, plastifier and additives takes place, whereas in the second zone the polymer is decomposed.

EXPERIMENT

Preparation of the experiment

For our experimental investigation, a single cylindrical rubber particle was used. For this purpose, a particle with a diameter of about 6 mm and a height of about 7 mm was prepared. The proximate analysis of the rubber is summarised in Table 1.

Tab. 1 Proximate analysis of a scrap rubber.

Proximate (wt%) analysis	
Moisture	0,1
Volatile matters	49,0
Fixed carbon	30,7
Ash	20,2

Experimental equipment

The combustion experiments were carried out in a set-up by applying the thermogravimetric method and using a single rubber particle. This system allowed to perform measurements for different experimental conditions, i.e., initial temperature, heating rate, mass of the particle, composition of the feed stream. The scheme of this experimental system is shown in Fig.1 and in detail described by Žajdlík [4,5,6].

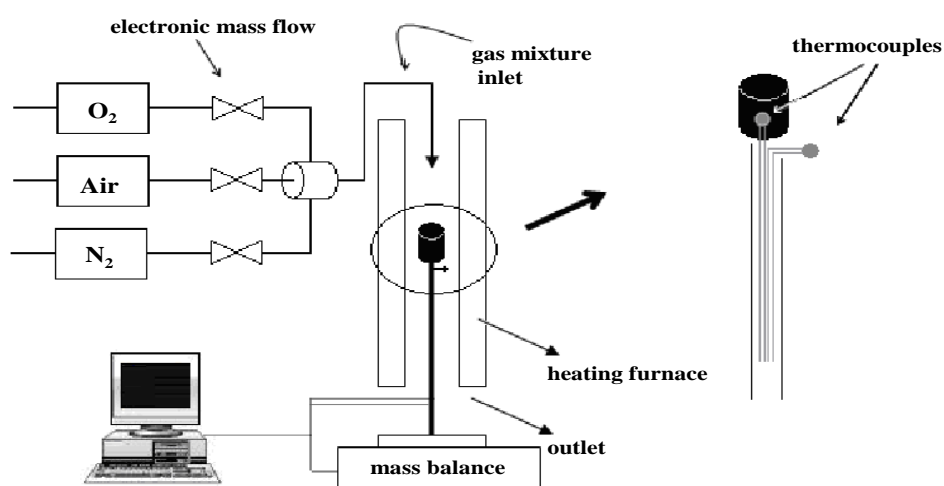


Fig.1 The experimental apparatus.

The single rubber particle was placed in the centre of the furnace tube using a thin ceramic rod. This rod was standing on a digital mass balance. The temperature in the centre of the rubber particle was measured by a thermocouple located inside the ceramic rod. The temperature of the gas phase was measured by a thermocouple placed below the rubber particle. Both the mass and the temperature of the particle were scanned with a frequency of 5 s. The

furnace consisted of an open ceramic tube. A programmer regulated the temperature inside the tube within the range of 20-1600°C. The feed gas stream with the desired content of oxygen in nitrogen was obtained by a system consisting of two calibrated electronic mass flowmeters.

To obtain ash from the rubber particle it was necessary to burn particles totally to a constant weight. The experimental conditions are given in Table 2.

Tab. 2 Experimental conditions for pyrolysis and combustion of a single rubber particle.

Temperature / °C	450 - 850
Pressure	atmospheric
Inlet concentration of oxygen / mol %	5 - 21
Weight of particles / kg	0.19×10^{-4} - 0.25×10^{-4}
Weight of degassed particle of rubber char / kg	10×10^{-4} - 15×10^{-4}
Particle diameter / m	6×10^{-3}
Particle height / m	7×10^{-3}
Flow-rate of the inlet gas / m^3s^{-1}	2.8×10^{-5}
Heating rate / °C min^{-1}	5

Pyrolysis and combustion of the particles

Three different experimental conditions were applied:

- 1) Pyrolysis at a heating rate of 5°C/min in flowing nitrogen (100 l/h), followed by combustion in air atmosphere at different initial temperatures: from 450°C to 850°C.
- 2) Pyrolysis at a heating rate of 5°C/min in flowing nitrogen (100 l/h), followed by combustion in a feed stream with different oxygen concentration and at different initial temperatures (Table 3):
- 3) The ignition temperature was investigated for different concentrations of oxygen and nitrogen in the inlet gas (Tab.3).

Tab.3 Feed stream compositions and initial temperatures for the combustion experiments.

oxygen [mol %]	nitrogen [mol %]	temperature [°C]
5	95	450, 650, 850
10	90	450, 650, 850
15	85	450, 650, 850

The experimental conversion (α_{exp}) was calculated according to Equation (1), where m_0 is the initial sample weight, m_i is the sample weight at arbitrary time and m_{final} is the final weight (the weight stable after combustion) - represented by the ash.

$$\alpha_{exp,i} = \frac{m_0 - m_i}{m_0 - m_{final}} \quad (1)$$

Characterisation of the pore structure

The internal pore structure of particles can be characterised by the following physical characteristics: specific surface area, specific volume of pores, pore size distribution and porosity. These quantities were determined by:

- the measurement of adsorption and desorption isotherms of nitrogen at the boiling point of nitrogen by applying the instrument SORPTOMATIC 1900 (Fisons Instruments, Milan Italy)

– mercury porosimetry using POROSIMETER 2000 (Fisons Instruments, Milan, Italy).

The sorption method was suitable for the identification of the microporous ($r_p < 2\text{nm}$) and mesoporous (between 2 – 50nm) structure; mercury porosimetry was applied for the determination of the macroporous ($r_p > 50\text{nm}$) structure and porosity.

RESULTS AND DISCUSSION

Our experiments could be divided into two main steps of processing waste rubbers: pyrolysis in a nitrogen flow and combustion in air atmosphere or in a mixture of nitrogen with oxygen.

Pyrolysis

The pyrolysis in nitrogen flow (100 l/h) at a heating rate of 5°C/min consists of two stages. The first stage proceeds at a temperature from 255°C to 360°C and the second stage at a temperature from 370°C to 500°C, as shown Fig.2.

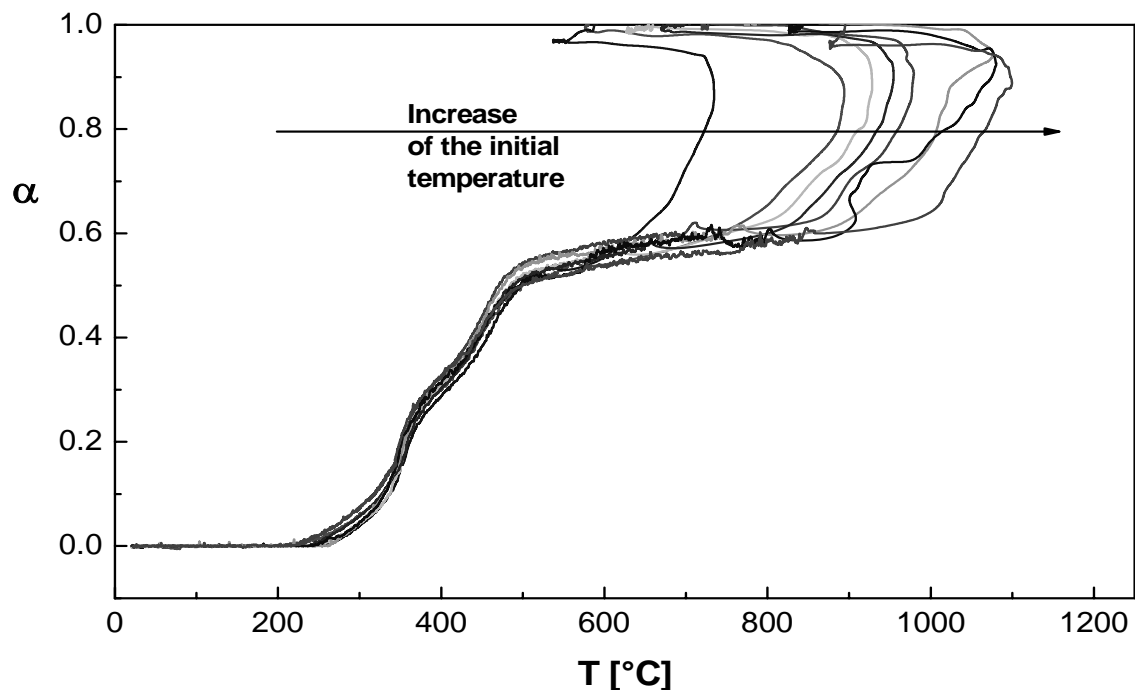


Fig.2 Conversion vs. temperature in the particle centre. The parameter of curves is the initial temperature increasing from 500°C to 850°C, with difference 50°C.

All pyrolysis experiments were carried out in the same mode. We can see that the development of the conversion with temperature in the particle was similar at various initial temperatures of combustion (Fig.2). The combustion started when the nitrogen flow was switched to the flow of air at different initial temperatures. Plasticators and additives from the rubber particle were released during the pyrolysis as gas or liquid. Throughout the first stage of pyrolysis, in the temperature range from 255°C to 360°C, compounds with lower

molar weights were released. During the second stage of pyrolysis, in the temperature range from 370°C to 500°C, aromatic and heavy hydrocarbons with a wide range of molar weights were liberated. The particle was totally devolatilized at temperatures higher than 500°C. Then, the particle contained only fixed black carbon and inorganic matter (ash). That means that during combustion of the particle at initial temperature lower than 500°C, two simultaneous processes proceed. Pyrolysis of residual volatile

matters and their immediate burn-out, coupled with the flame. A further burn-out of fixed carbon is initiated by the volatiles combustion. The primary volatiles combustion releases heat, and the particle is heated up to the ignition temperature of the fixed carbon.

In addition, the development of the internal porous structure during pyrolysis was investigated. Between the temperatures, 350°C and 550°C

macropores originate (Fig. 3), and above the range from 500°C to 550°C the internal surface in the microporous region grows two-fold (Fig. 4). The values of total porosity increase significantly from 0,31% to 32% at the end of pyrolysis (Fig. 5). The material of the particle does not provide mass transfer resistance (for oxygen flowing into the sample and for products of combustion flowing out of the sample).

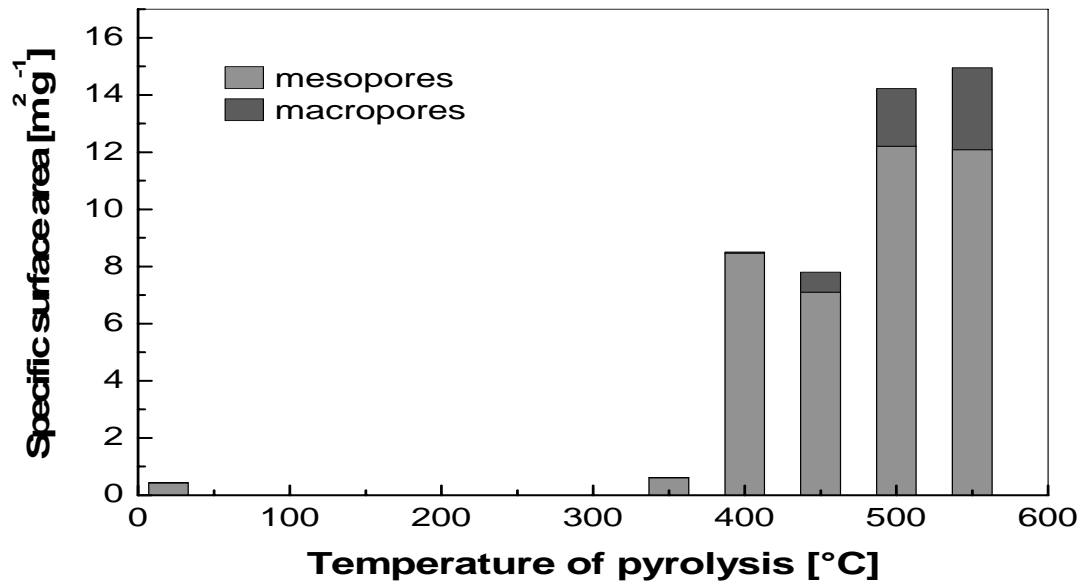


Fig.3 The development of the specific surface area with the degree of the pyrolysis process – pores detected by mercury porosimetry. The temperature means the point where the pyrolysis of a particular particle was stopped.

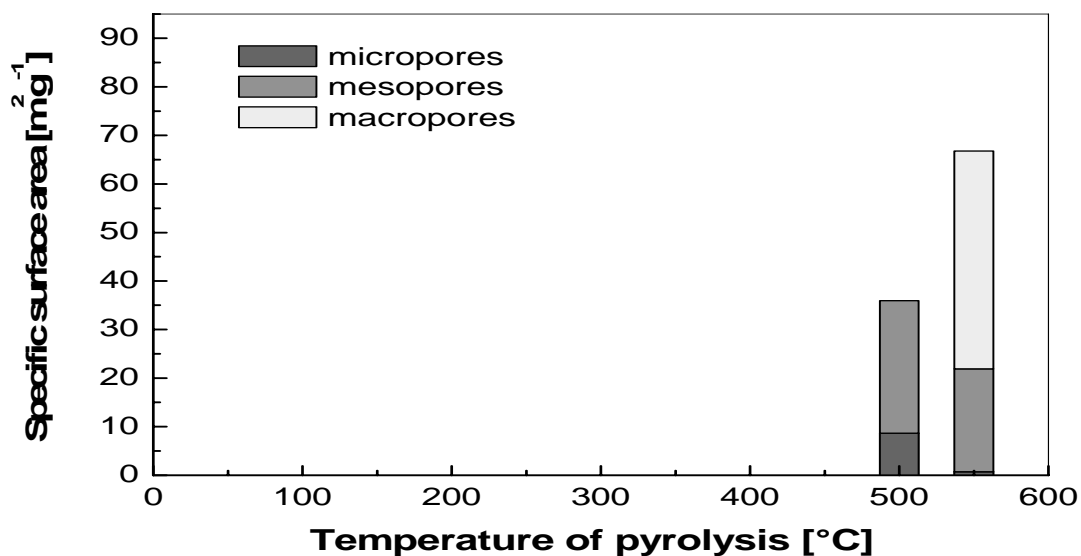


Fig.4 The development of the specific surface area with the degree of the pyrolysis process – pores detected by the sorption method. The temperature means the point where the pyrolysis of a particular particle was stopped.

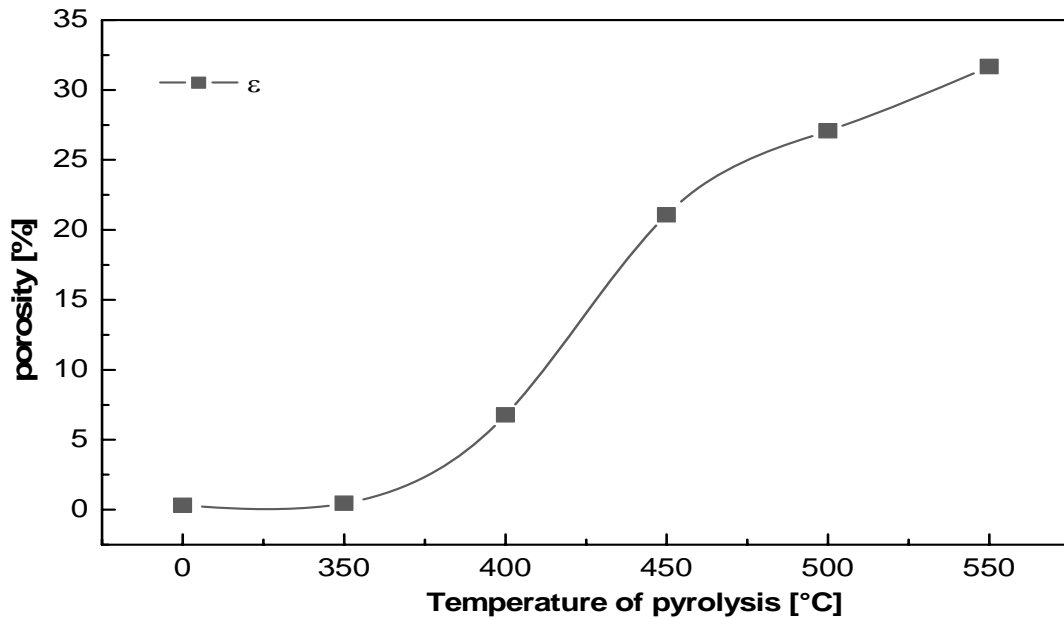


Fig.5 The development of porosity with different degrees of the pyrolysis process.

Combustion

Conversion of the rubber particle in air vs. time is shown in Fig. 6 and Fig. 7 at different initial temperatures of combustion. For the initial temperature 450°C the sample started burning at a temperature of 513°C (Tab.4). The combustion time, in the temperature range from 500°C to 700°C, decreases with increasing initial temperature. On the contrary, in the temperature range from

750°C to 850°C the combustion time increases. This fact could be the consequence of the combustion mechanism. A detailed study is necessary in the future.

The rubber particle, before and after combustion, is depicted in Fig.8. We can see that after combustion, the sample retained the shape of the original particle and consisted white ash.

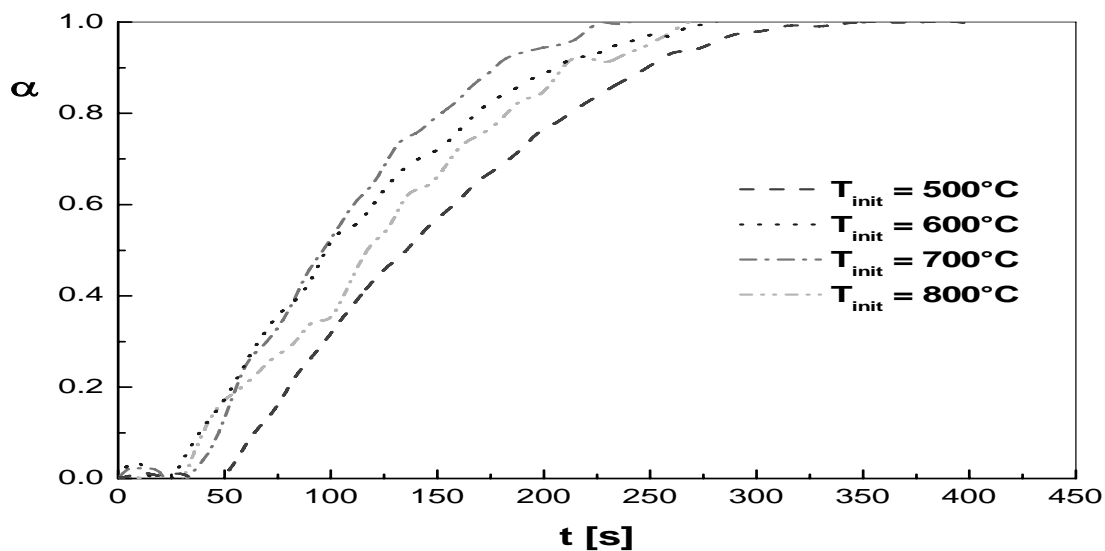


Fig.6 The dependencies of conversion α during the combustion of rubber particle in air atmosphere. The parameter of the curves is the initial temperature of combustion.

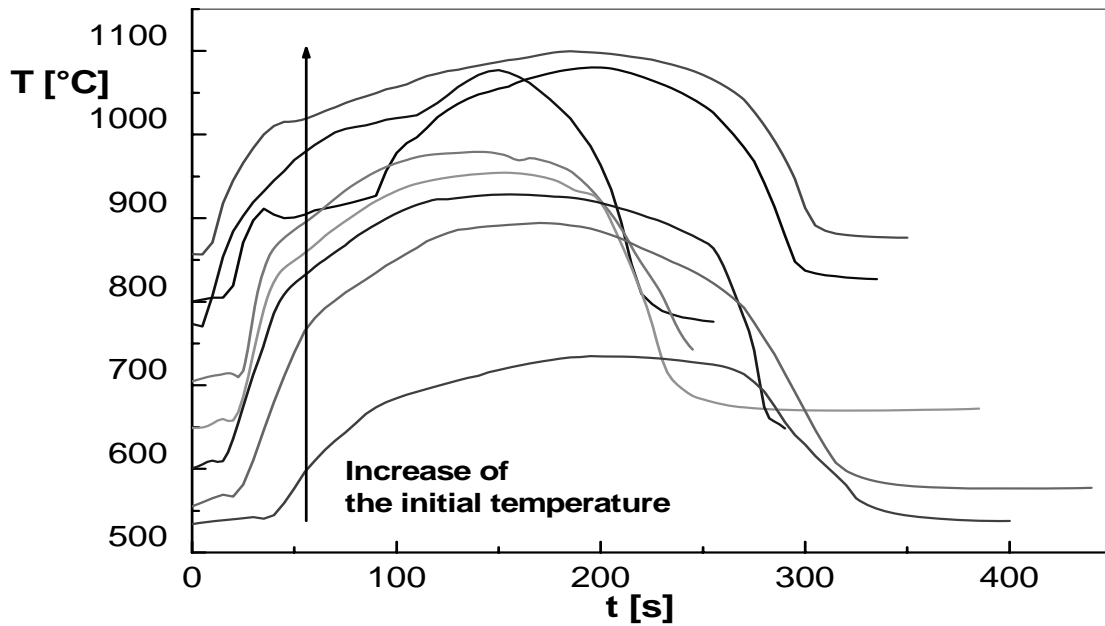


Fig.7 The dependencies of temperature in the centre of rubber during the combustion of rubber particle in air atmosphere. The parameter of the curves is the initial temperature of combustion increasing from 500°C to 850°C, with difference 50°C.

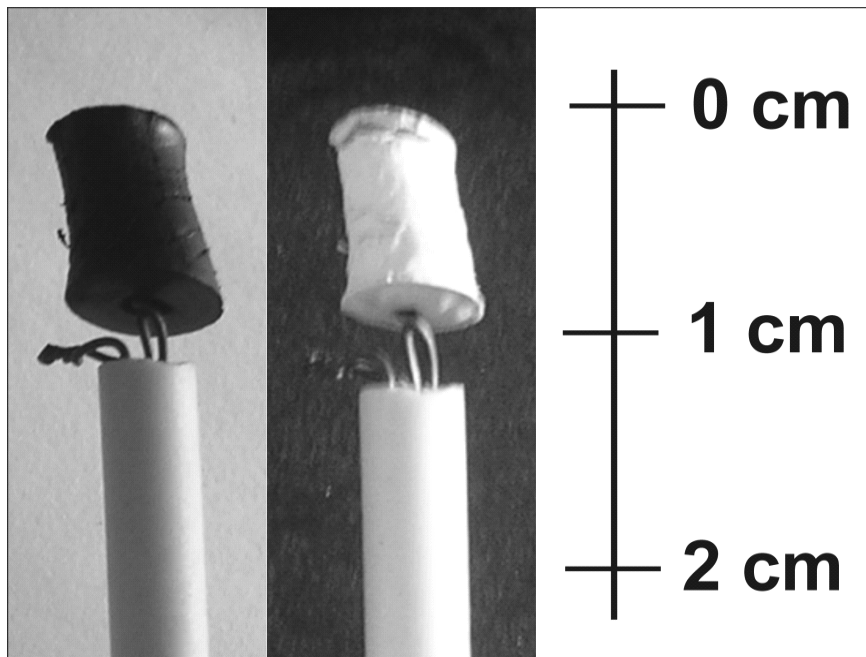


Fig.8 The rubber particle before combustion, and the ash obtained after total combustion of the same rubber particle in air atmosphere.

Combustion in the feed stream with different oxygen concentration

In the further experiments the behaviour of the rubber particle during combustion within a wide range of oxygen concentration was studied. We investigated the reaction time of

combustion of the rubber particle for different concentrations of oxygen in the inlet gas (5wt.%, 10wt.%, 15wt.% and 21wt.%) at different initial temperatures (450°C, 650°C and 850°C). In Fig.9 is

drawn the plot of different maximum available temperatures (y) vs. combustion time (x). The time of total combustion of the rubber particle at different initial temperatures and different concentrations

of oxygen in the inlet gas is shown in Tab.4. The combustion time declines with increasing content of oxygen in the feed stream and with growing initial temperature.

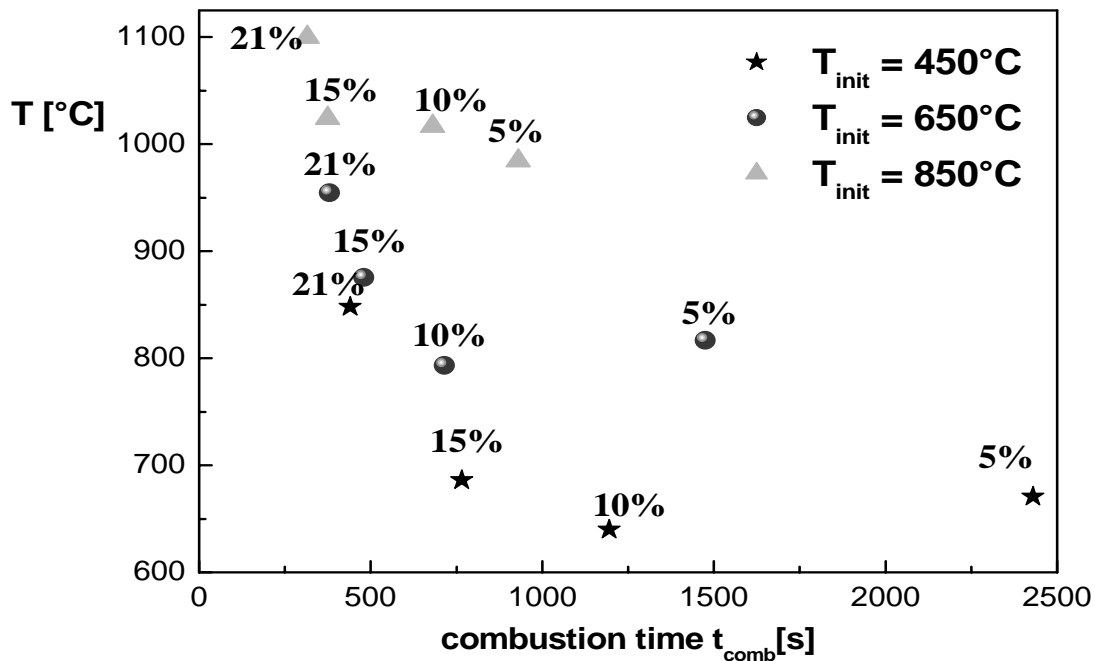


Fig.9 Combustion time vs. maximum available temperatures at different content of oxygen in the inlet gas at different initial temperatures of combustion.

Tab.4 Combustion time at different initial temperatures of combustion (t_{comb}) and ignition temperatures (T_{ignit}) at different content of oxygen in the initial gas.

oxygen content [mol %]	t_{comb} [s]			T_{ignit} [°C]
	$T_{init}=450^{\circ}\text{C}$	$T_{init}=650^{\circ}\text{C}$	$T_{init}=850^{\circ}\text{C}$	
5	2430	1475	930	551
10	1195	715	680	532
15	765	480	375	521
21	440	380	315	513

The ignition temperature

The ignition temperature was investigated experimentally, in the oxidation atmosphere. Furthermore, the influence of inlet concentration of oxygen on the ignition temperature of rubber particles was studied. It is evident that the ignition temperature is decreasing with increasing content of oxygen in the inlet gas, as shown in Table 4.

CONCLUSIONS

In the present paper, behaviour of a single rubber particle during thermal degradation was studied. It was found, that the pyrolysis consists of two stages, in which volatile components are released gradually. The result of this devolatilization is a change of the internal structure of the rubber particle in the

micro- and macro- regions of the pore size. Thus, the porosity increased from 0 to 32% and the specific surface area (pores detected by the sorption method) from 0 to $67\text{m}^2\text{g}^{-1}$. The different conditions for particle ignition were investigated, with initial temperature ranging from 500-700°C and initial concentrations of oxygen varying from 5 to 21 mol%. It was shown, that the combustion time depends on pyrolysis conditions. This fact can be caused by different pore structure development inside the particle. A more detailed research concerning the porous structure development during pyrolysis and combustion has to be performed.

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Symbols

m_0	initial sample weight, g
m_{final}	final weight, g
m_i	sample weight at any time, g
t	time, s
t_{comb}	total combustion time, s
T_{init}	initial temperature of combustion, °C
T_{ignit}	ignition temperature of combustion, °C
α	conversion
ε	porosity, %

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