Available online at <u>www.vurup.sk/pc</u> Petroleum & Coal <u>47</u> (2), 10-25, 2005

# INVESTIGATION OF TYRES AND COAL COMBUSTION IN A LABORATORY SCALE FLUIDIZED BED COMBUSTOR

Kristína Holíková, Ľudovít Jelemenský, Július Annus<sup>1</sup> and Jozef Markoš\*

Department of Chemical and Biochemical Engineering, Department of Technical Physics<sup>1</sup>, Faculty of Chemical and Food Technology, Slovak Technical University, Radlinského 9, 812 37 Bratislava, Slovakia corresponding author \*jozef.markos@stuba.sk

Received July11, 2005; received in revised form September 26, 2005; accepted September 28, 2005

### Abstract

Study of tyre and coal combustion in a laboratory scale fluidized bed reactor is presented. The combustion studies were performed with particles obtained from the Slovak brown coal (mine Handlová) and the scrap waste automobile tyres (EKO Beluša). Coal particle sizes of 0,51- 0,7 mm and the fraction of waste tyres 0.8 - 2 mm were used. The samples of coal and tyres with different weight ratios were combusted in a stream of air in a laboratory scale semi - batch fluidized bed reactor. As a fluidized bed, an inert material (ceramic spheres with a diameter of 0,4 - 0,63 mm) was used. The reactor was electrically heated to the initial temperature of 460°C -550°C inside the bed, and then it was charged with the samples of scrap tyres, coal or their mixtures. Three temperatures during the combustion were continuously monitored: temperature inside the bed, over the bed and the flue gas temperature, and its composition (oxygen, carbon monoxide and sulphur dioxide).

During the initial volatile phase combustion, a significant peak on the time dependence of oxygen concentration was detected in the experiments with tyres.

For the flue gases the dry limestone method (Ca/S  $\approx$  2) of desulphurization was used. The sulphur dioxide emissions fell down from 500 - 600 ppm to about 200 ppm for all samples.

Key words: Scrap tyres, coal, fluidized bed reactor, combustion and desulphurization

#### Introduction

One of the biggest problems facing mankind in the recent years is the environmental pollution resulting from industrial wastes, waste living materials, wastes from agriculture, etc. Particularly among the waste materials, concern about used tyres should not be ignored. The amount of used tyres is increasing more and more due to the increasing demand for tyres and because of their relatively short lifetime. The worldwide production of waste tyres amounts about  $5.0 \times 10^6$  tons per year, representing 2% of the total annual solid waste. The European Union produces more than 2.5×10<sup>6</sup> tons of used tyres per year, here is a very similar number for U.S., and for Japan it is one million tons annually <sup>[1, 2]</sup>. For example, the Slovak Republic is producing 940.000 new automobile tyres with an average increase of about 3% annually. Since 2002, one part of the waste tyres is treated to rubber granulates and then used as a substance for the manufacturing of sound insulation panels, road surfaces, railway crossings, micropore tubes or sport grounds. Based on the information obtained from the Bureau of Statistics in the Slovak Republic, the amount of bald motor-car and truck tyres is annually 12 300 tons only in Slovakia.

Most of the worldwide generated tyres (65.5 %) are simply dumped in the open or in landfill<sup>[3]</sup>. The *landfilling* is very common in these days, but the amount of the waste tyres is increasing faster and faster every year. The massive stockpiles possess fire and health hazard. Uncontrolled fires of the stockpiles are dangerous not only because of the high heat values production. The fires release a large amount of toxic pollutants <sup>[4]</sup>, containing zinc oxide, dioxins, volatile organic compounds, polycyclic aromatic hydrocarbons (PAH), carbon monoxide and other environmental and health hazardous matters. Some of these pollutants are potential carcinogens <sup>[5]</sup>. During the combustion of coal, the amount of released PAH strongly depends on the combustion conditions [6, 7]. The PAH emissions resulting from incomplete combustion should be reduced only during the controlled combustion by optimization of the process conditions. The total amount of PAH emitted follows a specific trend with the combustion temperature <sup>[7]</sup>.

Tyres are made of more than 100 different substances. The main components are rubber (ca. 50 wt%), fillers like carbon black or silica gel (25 wt%), steel (10 wt%), sulphur (1 wt%), zinc oxide (1 wt%) and many other additives like processing oil, plasticizer or vulcanization accelerators <sup>[8]</sup>. Polymer materials cannot degrade by themselves in general. Thus, they cannot be returned into the ecological environment through natural biological degradation, hydrolyzation or decomposition, like the biological materials. The main point of view is that raw material for the rubber industry is petroleum, especially in the countries where the natural rubber resources are out of reach. The global sources of petroleum are decreasing, so their appropriate utilization is needful. Therefore, it is necessary to develop methods for recycling or second disposal of the waste tyres.

Recycling of the waste rubber not only protects the environment (fire hazard of the stockpiles, place for breeding of mosquitoes, pests or rats), but includes also an important material recycle flow for tyre industry, petrochemistry or a rich energy source. The primary steps to recover worn out tyres include mechanical cryogenic grinding, scrapping or crushing. Waste tyres are shredded into various sized chips and granules with a wide possible usage. The powder rubber particles are considered to be used as an industrial raw material, for example for the filling of construction materials - mortar <sup>[9]</sup>, light weight aggregate in allowable fill <sup>[10]</sup> or as a rubberized concrete recommended for highway barriers <sup>[11]</sup>. All authors showed in their papers the rubber incorporation benefits and supposed a promising solution to improve the durability of cementbased structures. Fine powder rubber is widely used, mainly as a modifying agent for thermoplastic resin, an elastomer for improving the impact resistance of the materials, elastic material for elastic paving and functional composites which have the characteristics of safety, water permeability, soft ambulatory sense and water resistance <sup>[12]</sup>. The biggest disadvantage of these technologies of recycling is the high energy and liquid nitrogen consumption in the cryogenic mechanical grinding and shredding. Study about the health risk for the workers employed in the scrap-tyre shredding facilities [12] showed that airborne particulates of the working environment included mutagenic and thus potentially carcinogenic ingredients. The findings of this study reveal that the benefits of tyre-shredding may be partially offset by its disadvantage of imposing a health threat to processing workers <sup>[13]</sup>. However, the proportion of the recycling tyres remains negligible <sup>[9]</sup>.

It is well known that scrap tyres possess a high-volatile and low ash content, with a heat value higher than that of coal or biomass<sup>[1]</sup>. Therefore, the *thermal* treatment is a good way how to reuse the bald tyres and old rubber. The waste rubber conserves a large amount of energy, calorific value of approximately the  $3.3 \times 10^4$  kJ/kg, and if the waste rubber is not recycled the theoretical value of lost heat will reach 3.0×10<sup>14</sup> kJ worldwide <sup>[14]</sup>. Thermal processes could be in general subdivided into combustion (incineration). gasification and pyrolysis of waste tyres. They all have the following advantages:

• the volume of the waste can be reduced by more than 90%,

• net energy producer with possible material recovery, and

non-polluting and capable of destroying most of the organic substances, which are harmful to human health <sup>[5]</sup>.

On the other hand, the problems attached with the thermal treatment of waste tyres are:

• Disposal of the ash: lead and cadmium salts, used as stabilizers in the tyre production, remain as ash, thus causing disposal problems.

Toxic gases: when tyres are burnt, some toxic gases like  $SO_2$ ,  $H_2S$ , HCI, HCN, etc. are generated, thus requiring additional systems for their proper treatment.

• Soot: produced by imperfect burning of tyres. In general, both further combustion and high flame temperature are necessary.

• Appropriate incinerators and combustors: due to the corrosive action of the flue gases, higher temperatures and insufficient oxygen supply are necessary. It is important to design combustors with the application of appropriate chemical and mechanical materials<sup>[5]</sup>.

The pyrolysis process accounts for higher energy recovery values than incineration (70 % vs. 41%)<sup>[5]</sup> and is also environmentally very attractive. Thermal decomposition of waste tyres in oxygen-free atmosphere leads to gaseous, liquid and solid products in general. The amount and composition of pyrolysis products depends on the kind of polymers contained in the original tyre, on the temperature <sup>[15]</sup>, and the heating rate <sup>[8]</sup> of the process. Gaseinclude ous products could noncondensable gases as H<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, CO,  $CO_2$  and organics such as  $C_1 - C_6$  alkanes and  $C_2$  olefins <sup>[15]</sup>. The gases evolved during pyrolysis are mostly composed of light combustible hydrocarbons which could be used as a supplementary heating resource in the pyrolysis processes <sup>[16]</sup>. The liquidoil phase contains valuable compounds. however their separation from the complex liquid mixture is still difficult now. Due to its caloric value, the oil valorization directly as a fuel is always possible. Another possible usage of the oil pyrolysis products is as a feedstock for the petroleum refinery as a

source of petrochemicals. The obtained solid product <sup>[16]</sup> could be easily separated from the steel cords and be converted into a fine powder. Thermophysical and combustion properties of the tyre-char are in a good agreement with those of coal dust. So, the co-combustion of coal and tyrechar is possible in a coal dust power plant, without any burner modification <sup>[16]</sup>. The physical properties (porosity, particle and aggregate size, surface area), chemical properties (elemental analysis, ash content and composition) and aqueous adsorption properties (for metals, phenols and for example methylene blue) predetermined the pyrolytic char to active char production [12].

Detailed distributions of products from pyrolysis at different temperatures for two different types of tyres are summarized in study <sup>[15]</sup>. No strong effect of temperature on the product distribution for the both samples was observed. No significant influence of three commonly used tyre additives (zinc oxide, sulfur and carbon black) was found on the DTG curves for used reference rubbers <sup>[8]</sup>.

However, many technical and operational problems must be solved before the pyrolysis will be safety and economically profitable. From the comparison of different disposal options available, pyrolysis has a promising future <sup>[5]</sup> because of the possible utilization of all pyrolysis products <sup>[15]</sup>.

Another possible utilization of the waste tyres and rubbers is *combustion*. As it was mentioned above, it is convenient to combust a solid product of pyrolysis with coal dust without any changes in conventional combustors <sup>[16]</sup>.

During the combustion of tyres and coal the contained sulphur is released and converted into gaseous pollutants such as  $SO_2$  and a little bit of  $SO_3$ . These oxides are harmful for the environment - acid rains and creation of health impacts on population were observed. Conclusions about sulphur oxides in flue gases varied from study to study.

Courtemanche and Levendis investigated co-combustion of coal with plastics and tyres in a laboratory scale FBC <sup>[17]</sup>. Samples were combusted in air and a nitrogen free atmosphere at a temperature range of 1300 –1600K. The SO<sub>2</sub>, CO, NO<sub>X</sub> and CO<sub>2</sub>

concentrations were also measured. NO<sub>x</sub> emissions were detected four times higher for coal as for scrap tyres and ten times higher as for plastics. A study supported formation of NO<sub>x</sub> from air nitrogen at these temperatures. Combustion of coal in air produced 20% more NO<sub>x</sub> than in a nitrogen free atmosphere. Generation of  $SO_2$ emissions was found as a function of sulphur content in the fuel. CO emissions dramatically increased for fuel-rich and were negligible for fuel-lean mixtures <sup>[17]</sup>. The coal co-combustion with the waste plastics and tyres appears to be a promising technology for reduction of NO<sub>x</sub> emissions. However, the pulverizing of the plastics and tyres is still not cost-effective. Authors Prisciandaro et al., [18] performed a long-term study of the technical feasibility of alternative fuels in the clinker production process. The results were demonstrated on real plant data: shredded tyres and waste oils were used as alternative fuels with a pet coke in clinker kilns of two different cement plants. In the case of pet coke with tyres, the emissions of all regarded gases (NO<sub>X</sub> CO and SO<sub>2</sub>) increased, but the level was still under the permitted limits of the European Union. For the mixture of pet coal with the waste oil, the emission of monitored gases decreased in general <sup>[18]</sup>.

Calcium carbonate and calcium hydroxide are the most widely used additives for SO<sub>2</sub> adsorption from flue gases during combustion. These may be incorporated directly into the fuel or introduced into the gas stream immediately beyond the combustion zone. Crushed calcites are obviously the cheapest additive available for sulphur removal. Sometimes the greater efficiency of Ca (OH)<sub>2</sub> can be sufficient to offset its higher cost <sup>[19]</sup>.

The aim of this paper is to investigate the possibility of coal and tyres combustion in a laboratory scale fluidized bed reactor and to compare their behaviour during combustion. The second aim was to test the common dry desulphurization method with the limestone as additive for desulphurization of the flue gases released by combustion of tyres.

#### Experimental

#### Feed materials

Coal particles were prepared from brown coal (mine Handlová, Slovakia) by grinding and meshing to sizes 0.5 - 0.71 mm. Scrap tyres were supplied by the rubber recycling enterprise EKO Beluša in Slovakia. Samples were shredded. crumbed and meshed to produce a size of 0.8 - 2 mm. The scrap tyres did not contain steel thread and textile netting. The proximate analysis of the coal and scrap tyres (based on the TG experiment) and ultimate analyses of coal (estimated by the mine laboratory), limestone (estimated by Považská cementáreň, JSC, Ladce, Slovakia) and scrap tyres are summarized in Tab. 1.

Tab. 1 Proximate and ultimate analyses of coal (Handlová mine), scrap tyres (EKO Beluša, s.r.o.) and ultimate analysis of limestone (Považská cementáreň, J.s.c, Ladce)

Property	COAL	TYRES	Property	COAL	TYRES
C <sup>daf</sup>	72.75	81.24	Moisture	8.74	1.72
H <sup>daf</sup>	5.33	7.36	Volatile matter	32.96	61.61
N <sup>daf</sup>	0.9	0.49	Fixed carbon	44.21	22.66
S <sup>daf</sup>	2.41	1.99	Ash	14.09	14.01

Ultimate analysis [wt%]

Proximate analysis [wt%]

Ultimate analysis [wt %]					
LIMESTONE					
CaCO₃	80.41	TiO <sub>2</sub>	0.192		
MgCO <sub>3</sub>	1.75	MnO	0.046		
Al <sub>2</sub> O <sub>3</sub>	12.84	CI	0.0082		
Fe <sub>2</sub> O <sub>3</sub>	1.014	$P_2O_5$	0.01		
K <sub>2</sub> O	0.543	Na <sub>2</sub> O	0.04		

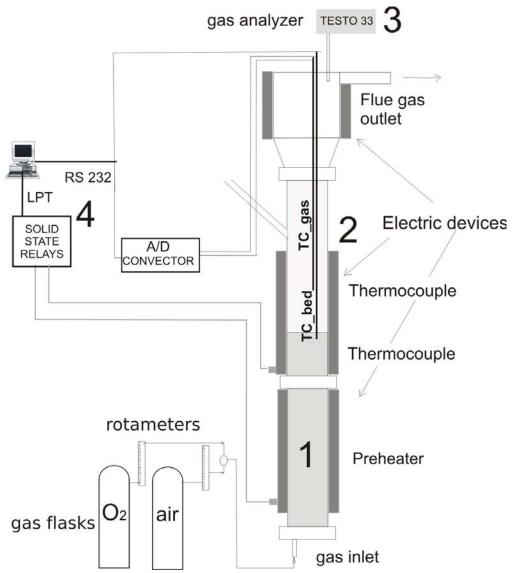
#### Experimental apparatus

The pyrolysis experiments were carried out in an equipment using the TGA principles <sup>[20]</sup>. A steel net was filled with a scrap tyre sample and then placed in the centre of the furnace tube using a thin ceramic rod. The single coal particle was stacked on the ceramic rod. The rod was standing on a digital mass balance. The temperature in the centre of the particle was measured by a thermocouple placed inside the ceramic rod. Both the mass and the temperature of the particle were measured with a frequency of 20 seconds. The furnace consisted of an open ceramic tube. The temperature inside the tube was regulated within the range of 20 -1600°C by a programmer. The feed stream was nitrogen.

For the *combustion* of coal and tyres, a semi-batch fluidized bed reactor was constructed. The reactor consisted of three main parts: (1) gas mixer and preheater, (2) combustor chamber, (3) gas analyzer and (4) instrument and control panel (Fig. 1). The gas mixer was a 218 mm high tube; the combustor chamber was a 380 mm high tube. Both tubes had the same internal diameter of 51 mm. The gas mixer was filled with ceramic saddles, used as pre-heater. The gas distributor plate was made of a stainless steel net

without any pressure drop. The combustor height from the distributor to the gas outlet was 0.74 m. All three sections were heated by external electric devices (together 2kW, Fig. 2). The temperatures were regulated through an A/D convector with on-off regulators. The temperature profiles along the combustor were measured with two K-type (chromel - alumel) thermocouples 0.03 and 0.13 m above the gas distributor. The temperature of the flue gases was measured by a thermocouple equipped with a gas analyzer (TESTO 33). As fluidized bed an inert material (ceramic spheres with a particle size of 0.41-0.63 mm and the overall mass of 100 g) was used. The fixed bed of inert material had a height of about 5 cm. The minimum fluidization velocity was investigated in the geometrically same glass tube for all kinds of samples. The pressure drop in the fluidized bed was measured at ambient temperature (20°C) and atmospheric pressure. The volumetric flow rate of air was kept constant referred to 20°C, atmospheric pressure for each experiment (Tab. 2).

The flue gas composition was measured by a gas analyzer (TESTO 33 by TESTO AG GmbH &Co., Germany). Oxygen was measured in volume percentage; carbon monoxide and sulphur dioxide were detected in ppm.



**Fig. 1** Schematic diagram of the fluidized bed combustor (1- gas mixer and preheater, 2- combustor chamber, 3- gas analyzer, 4- instrument and control panel)

#### Experimental procedure

#### Pyrolysis of scrap tyre and coal

The TGA diagrams were expressed as time dependences of the weight loss of coal and tyre samples during drying and devolatilization in nitrogen atmosphere. Coal and tyres were devolatilized by the same procedure consisting of following steps:

1. Drying in flowing nitrogen (100 I hod<sup>-1</sup>) at 100°C for 3 hours.

2. Devolatilization, which ensured the removal of volatile substances by heating to a temperature of 800°C in flowing nitrogen (100 I  $h^{-1}$ ). The heating rate was 100°C/hour and 200°C/hour at the heating temperatures up to 600°C and 800°C, respectively.

Based on the weight loss at different temperatures we were able to specify the content of moisture, volatiles and fixed carbon. After complete pyrolysis, the sample was combusted to a constant weight of the ash.

#### Fluidization characteristics

Initial experiments were carried out in the geometrically same glass tube to identify the minimum fluidization velocity for the samples. The development of the pressure drop for the coal-inert (Fig. 2) and coal-inert-tyre (Fig. 3) mixtures was measured.

Minimum fluidization velocities for these mixtures were determined graphically.

The hydrodynamic changes resulting from the addition of small weight quantities of coal particles in the inert caused a decrease in the minimum fluidization velocity. This minimum fluidization velocity was lower for samples with 3 and 6 g of coal against the inert bed material. For 9 g of coal sample with inert, the minimum fluidization velocity increased again. The same effect was observed for the mixture of coal and tyres in the inert material (Fig.3).

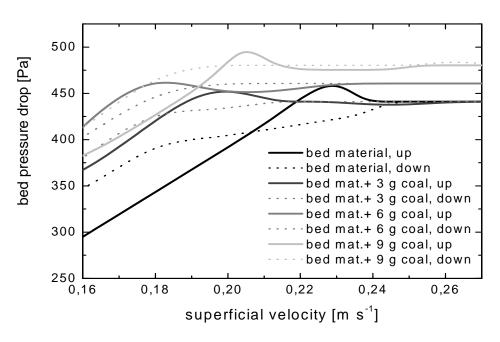


Fig. 2 Development of pressure drops for inert particles (100 g) together with coal particles.

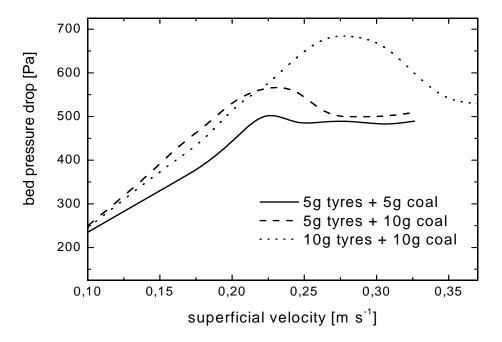


Fig. 3 Development of pressure drop for inert particles (100g) together with coal and tyre particles

#### Combustion experiments

Coal and scrap tyre particles (Tab.2) were fed into the batch reactor after reaching the initial temperature ( $460^{\circ}$ C -  $550^{\circ}$ C) inside the bed. Then, air was switched on and the fluidization, devolatilization and combustion processes started. The experiment accomplished when the oxygen concentration again reached 21 vol.%.

 
 Tab. 2
 Mass and ratio of the samples and air bulk flow used in combustion experiments

Weigh	nt ratio	Air flow [dm <sup>-3</sup> min <sup>-1</sup> ]	Sample
Scrap	Coal		weight
tyres	Cuar		[g]
1	0	24	10
3	2	26	10
2	1	26	10
1	1	26	10
2	3	26	10
0	1	26	10

#### Desulphurization experiments

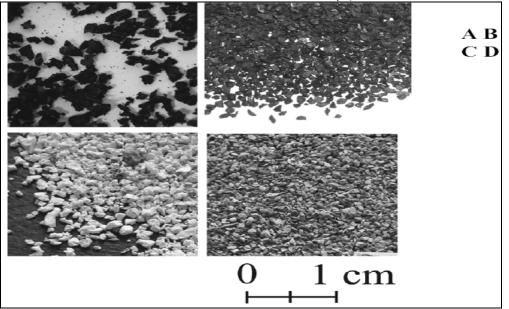
In the desulphurization experiment the tyre-coal ratios 1:0, 1:1 and 0:1 were used in the sample composition. The amount of the domestic limestone (Považská Cementáreň, JSC, Ladce, Slovakia) was defined by the Ca/S ratio  $\approx$  2,0. The reactor was charged with a sample mixed with limestone at the initial temperature of 460°C.

#### **Results and discussion**

# Thermogravimetric analysis of the scrap tyres and coal

The weight loss of the coal sample reveals that the coal contains almost 10 wt% of humidity and 33 wt% of volatiles (of a wide range of molecular weight) released consecutively by increasing the temperature up to 800°C (Fig. 5). Combustion of the devolatilized sample to a constant weight provides about 14 wt% of ash (Tab.1). Pyrolysis of the tyre sample in a nitrogen stream consists of two-stages (Fig. 5). Fig.6 B reveals a short and insignificant first stage proceeding in the temperature range between 280-350°C. The second sharpest weight loss was detected in the temperature range from 350°C to 480°C. The release of volatiles from the tyres should proceed simultaneously or consecutively depending on the source and the composition of the considered tyre sample. Hence, the shape of the pyrolysis curves is different from tyre to tyre.

**Fig. 4** Photo of scrap tyre particles (A), coal particles (B), ash from the tyres (C) and coal (D)



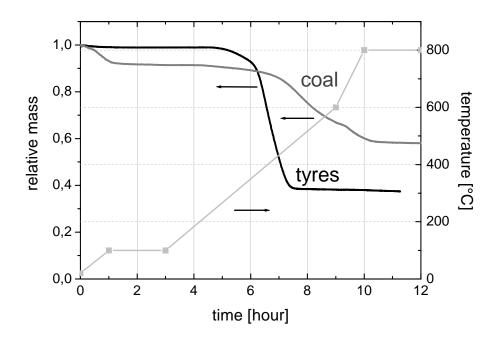
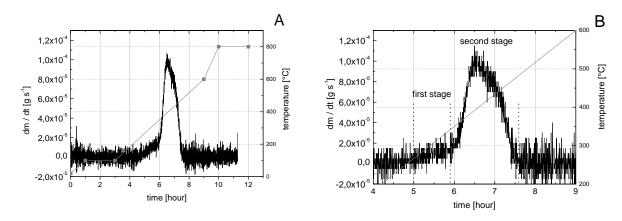
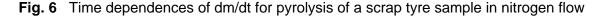


Fig. 5 Weight loss during the pyrolysis of coal and tyre sample in nitrogen flow

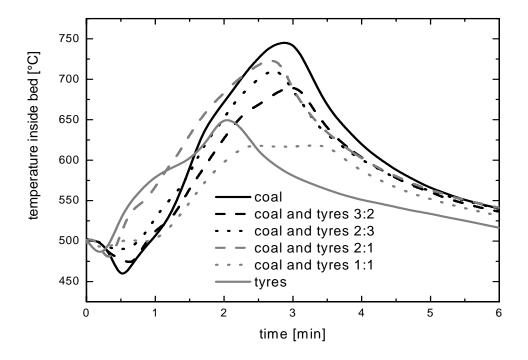




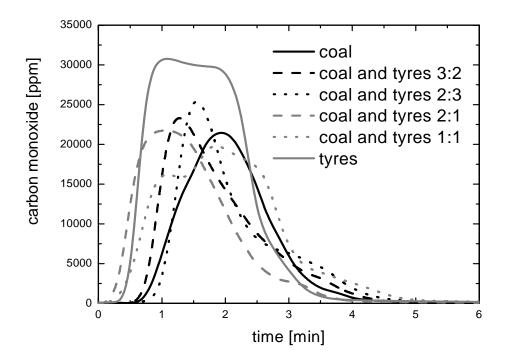
#### Combustion of scrap tyres and coal in FBC

Immediately after charging the reactor with the sample, a short explosion occurred. This explosion could be explained by a rapid release of volatiles from the tyre particles. The temperature of the flue gases increased by 40°C in 15 seconds for samples containing tyres (Fig. 7). The combustion of volatiles was incomplete because of their short residence time in the reactor. In the stack, heavy smoke

was observed immediately after the explo-This smoke contained nonsion. combusted volatile matters from the tyre sample. Incomplete combustion was detected also in the carbon monoxide emissions (Fig. 8). A fast release of volatiles from tyres might have cause particles fragmentation and subsequent acceleration of their combustion. In comparison, coal volatiles and char burned out slowly; also, the CO emissions were lower for coal (Fig.8).



**Fig. 7** Time dependences of temperature inside the bed during combustion of coal and tyre mixtures at the initial temperature of 500°C

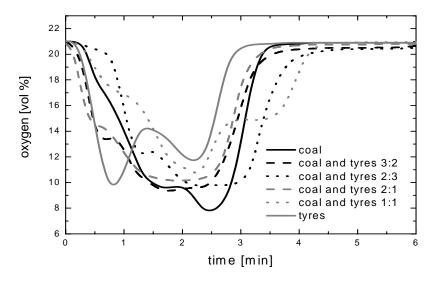


**Fig. 8** Time dependences of carbon monoxide emissions in the flue gas during combustion of coal and tyre mixtures at the initial temperature of 500°C

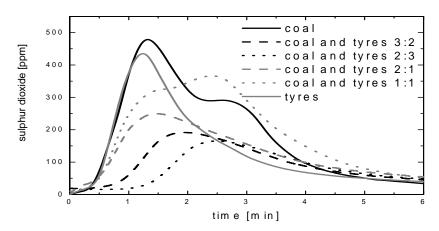
The DTG curve (Fig. 6) showed that most of the volatiles were released from tyres at a temperature ranging from 350 to 480°C at the initial temperature of combustion of 500°C. A release of volatiles was expected immediately after charging the reactor with the sample. Furthermore, an intensive initial pyrolysis was supposed with the associated large volatiles flames <sup>[4]</sup>. This explosion was confirmed by the sound originated during the pyrolysis in the reactor. This sound was like a sound of flame in a closed space. The preheating of the environment in the reactor accelerated combustion of the coal volatiles, and consumption of oxygen increased more than in the case of a pure tyre sample. In combustion of an equivalent coal-tyre mixture the loudest explosions occurred.

The rich tyre sample combustion could be divided into two significant stages (Fig. 9, 11). In the first stage, both burnout of volatiles and a decrease in oxygen con-

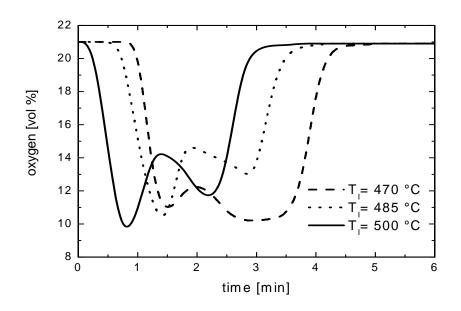
centration are faster than for the coal samples. The first peak in the oxygen concentration (Figs. 9, 11) is observed after the explosion and the resulting combustion of the released fractions of volatiles (both for the pure tyre and the coal-tyre mixture sample). After the burnout of volatiles in the first phase a small period followed, where the volatiles residues and black char were heated up, and a weak combustion might have taken place <sup>[4]</sup>. The simultaneous burn-out of the solid carbon within the secondary volatiles flame from burning volatiles residue is not exactly in agreement with the TGA results discussed earlier. It is a possible explanation of the two visible peaks in the oxygen concentration profile.



**Fig. 9** Time dependences of oxygen concentration in the flue gas during combustion of coal and tyre mixtures at the initial temperature of 500°C



**Fig. 10** Time dependences of sulphur dioxide emissions in the flue gas during combustion of coal and tyre mixtures at the initial temperature of 500°C



**Fig. 11** Time dependences of oxygen concentration during combustion of scrap tyres at different initial temperatures

Initial explosion of volatiles from a single coal sample does not exist. Particles after the batch charge are preheated slowly by the inlet gas and inert bed material. Combustion of the released volatiles and the start up of the char combustion is longer than for the tyre sample. The amount of fixed carbon is a little higher than the amount of volatiles, thus coal burns out more slowly than tyres. Hence, the release of volatiles is slow and the preheating of the particle by the volatiles combustion is comparably slow as in the tyre experiments. The initial phase is longer; moreover, the combustion is uniform, as it could be seen in the concentration profile of oxygen (Fig. 9).

Sulphur is used as a vulcanization agent and takes place in the linking bridges over the macromolecules of rubber. With regard to the presence of sulphur links of vulcanized rubber structure, emissions of sulphur dioxide were expected <sup>[17]</sup>. The oxidation of sulphur from the tyres was examined especially at the time when the volatiles were burned out (Fig. 10). The black carbon in tyres burned out without a significant effect on the SO<sub>2</sub> emissions (Fig.10). On the other hand, in the experiments with coal, practically all SO<sub>2</sub> is generated through the time of combustion, because sulphur is integrated into the coal char structure. SO<sub>2</sub> emissions

detected in the case of the coal-tyre combustion are approximately the sum of the values obtained from experiments with one-component samples (Fig.10).

The start up of the coal combustion is slow, but the increase in temperature inside the bed is very high. Development of the temperatures for the mixture of both materials is again approximately the sum of the values for the single samples (Fig. 7). The increase in temperature values above the bed is lower than inside the bed. This could indicate that combustion takes place inside the bed and not on its top. A short-time increase in temperature above the bed in the case of coal-tyre mixture characterized the explosion, which caused a movement of the reaction zone from the bottom of the FBC to the whole volume. The increase in temperature of the flue gas for a short time was also detected. During some experiments the explosion was so smash, that the reaction zone occupied the whole volume and displaced oxygen from the reactor. The fire blew out from the reactor and ran until all volatiles from the sample flowed out from reactor.

In the following figures, we can see a comparison of combustion of pure tyre samples in a semi-batch fluidized bed reactor at three different initial temperatures, 470°C, 485 and 500°C. At the temperature of 500°C, the combustion, represented by a decrease in the oxygen concentration, started immediately after charging the reactor (Fig. 11). Of course, a higher initial temperature caused an earlier start up of the combustion. The concentration of oxygen decreased, the concentration of SO<sub>2</sub> and CO increased (Figs. 12, 13). Two stages of combustion are observed in the time dependences of oxygen. Volatiles are pyrolysed at first with associated flames (the sound in the reactor was assigned to the flames inside). After the volatiles burnout phase, a low-intensity period followed, where residue volatiles were burned out, the char was preheated-up and a slow combustion took place. Then, the carbon black burned out and the second stage took place. This phenomenon was explained in the previous part. At the temperatures 500°C and 485°C the first stage was more intensive than the second one. At the temperature 470°C, the second stage was more intensive, oxygen consumption and CO emissions were higher as in the cases of higher temperatures. The stages of combustion for volatiles and char were strictly isolated.

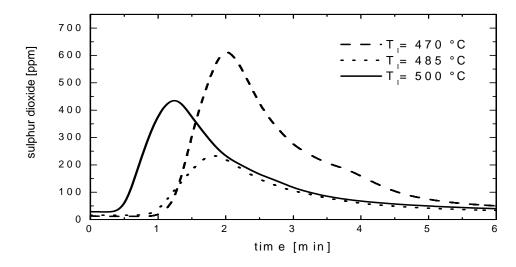


Fig. 12 Time dependences of sulphur dioxide emissions during combustion of scrap tyres at different initial temperatures

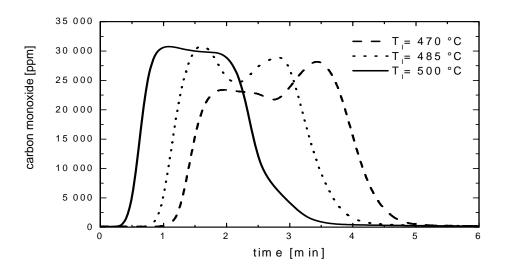


Fig. 13 Time dependences of carbon monoxide emissions during combustion of scrap tyres at different initial temperatures

# Desulphurization of the flue gas by the dry limestone method

Compounds containing sulphur (in their structure gaseous pollutants, mainly SO<sub>2</sub>) are released during combustion. As it was mentioned in our previous text, the vulcanized tyres contain sulphur links, values of the sulphur mass fraction are approximately equal to the values of the coal used (Tab. 1). During the combustion of volatiles from the tyres, sulphur is released and causes sulphur dioxide emissions. In our experiments, the dry limestone method was used (with the Ca/S ratio equal to 2) for desulphurization. The emissions of  $SO_2$  drop more than twice (Figs.12 and 15) for the coal sample and three times in the case of a coal-tyre mixture. As it was mentioned in the previous chapter, the emissions of  $SO_2$ are strongly dependent on the sample type. Sulphur links in the tyres were converted into  $SO_2$  during the combustion of volatiles. The development of sulphur dioxide emissions from the coal-tyre mixture was the sum of developments in the single samples, as it was mentioned above. This behaviour was supported also in the experiments with additives (Fig. 15).

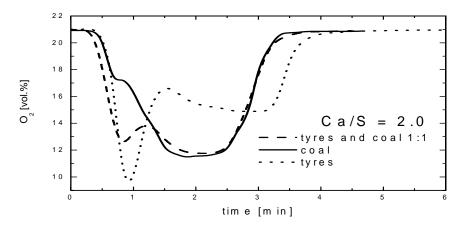
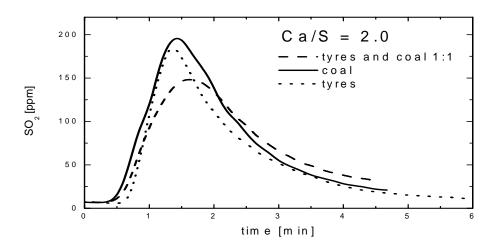


Fig. 14 Time dependences of oxygen concentration in the flue gas during combustion with an additive (limestone) for different samples



**Fig. 15** Time dependences of sulphur dioxide emissions in the flue gas during combustion with an additive (limestone) for different samples

## Conclusion

An experimental study of pyrolysis and combustion of coal and scrap tyres was presented. The pyrolysis experiments were carried out in an apparatus by applying the TGA method. The combustion was performed in a laboratory scale fluidized bed combustor. The dry method was applied for desulphurization of the flue gas during combustion.

The results of our work could be summarized in the following items:

- Pyrolysis of the tyres proceeded in nitrogen flow at a temperature ranging from 280°C to 480°C. Two stages of pyrolysis were detected on the dm/dt curve.
- A semi-batch laboratory scale fluidized bed reactor was designed and constructed. A study of coal and tyres combustion was performed.
- Carbon monoxide emissions are very high and it is necessary to extend the retention time of the flue gas in the reaction zone at the temperature above 750°C. The re-

construction of the reactor will be necessary in the future.

- The tyre combustion was characterized by two significant stages. The first stage was accompanied with an explosion of volatiles.
- Combustion of tyres at higher temperatures had an earlier start up.
- The dry desulphurization method is more suitable for desulphurization of the coal – tyre mixture in comparison with the pure tyre sample.

**Acknowledgement:** This project was supported by the Grant VEGA No. 1/0064/03 from the Slovak Scientific Grant Agency

SYMBOLS:

daf FBC	dry ash free fluidized bed combustor
m	mass, g
t	time, s
Tc_bed	temperature inside the fluidized bed, °C
Tc_gas	temperature of gas above the fluidized bed, °C

## **REFERENCES**:

- 1. Berrueco, C., Esperanza, E., Mastral, F.J., Ceamanos, J. and García-Bacaicoa, P., Journal of Analytical and Applied Pyrolysis, (2005), 74(5), 245 - 253.
- 2. Rodriguez, I. de M., Laresgoiti, M. F., Cabrero, M. A., Torres, A., Chomon, M. J. and Caballero, B., Fuel Processing Technology, (2001), 72(1), 9-22.
- 3. Roy, C., Chaala, A. and Darmstad, H., Journal of Analytical and Applied Pyrolysis, (1999), 51(1-2), 201-221.
- 4. Atal, A. and Levendis, Y.A., Fuel, (1995), 74(11), 1570-1581.
- 5. Sharma, V. K., Fortuna, F., Mincarini, M., Berillo, M. and Cornacchia, G., Applied Energy, (2000), 65(1-4), 381-394.
- 6. Mastral, A. M., Callén, M., Murillo, R. and Garcia, T., Fuel, (1998), 77(13), 1513-1516.
- 7. Mastral, A. M., Callén, M. and Murillo, R., Fuel, (1996), 75(13), 1533-1536.
- 8. Seidelt, S., Muller-Hagedorn, M. and Bockhorn, H., Journal of Analytical and Applied Pyrolysis, (2005), In press,
- 9. Yang, H. S., Kim, D. J., Lee, Y. K., Kim, H. J., Jeon, J. Y. and Kang, C. W., Bioresource Technology, (2004), 95(1), 61-65.
- 10. Pierce, C. E. and Blackwell, M. C., Waste Management, (2003), 23(3), 197-208.
- 11. Topcu, I. B. and Avcular, N., Cement and Concrete Research, (1997), 27(12), 1893-1898.
- 12. Fang, Y., Zhan, M. and Wang, Y., Materials & Design, (2001), 22(2), 123-128.
- 13. Chien, Y. Ch., Ton, S., Lee, M. H., Chia, T., Shu, H. Y. and Wud, Y. S., The Science of the Total Environment, (2003), 309,35-46.
- 14. Helleur, R., Popovic, N., Ikura, M., Stanciulescu, M. and Liu, D., Journal of Analytical and Applied Pyrolysis, (2001), 58–59,813–824.

- 15. Ucar, S., Karagoz, S., Ozkan, R. and Yanik, J., Fuel, (2005), In press), 1-9.
- 16. Napoli, A., Soudale, Y. and Castillo, S., Journal of Analytical and Applied Pyrolysis, (1997), 40-41,373-382.
- 17. Courtemanche, B. and Levendis, Y. A., Fuel, (1998), 77(7), 183-196.
- 18. Prisciandaro, M., Mazziotti, G. V. and Veglió, F., Resources, Conservation and Recycling, (2003), 39,161-184.
- 19. Brady, M. E., Burnett, M. G., Galwey, A. K., Murray, O. and Sharkey, R., Fuel, (1994), 73(3), 329-333.
- 20. Jelemenský, L., Remiarová, B., Žajdlík, R. and Markoš, J., Petroleum and Coal, (1999), 41(2), 85-90.