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COMPARISON OF MATERIAL BALANCE OF FINAL PRODUCTS FROM A PYROLYSIS PROCESS

SROVNÁNÍ MATERIÁLOVÉ BILANCE VÝSTUPNÍCH PRODUKTŮ Z PYROLÝZNÍHO PROCESU

Abstract

Recently thermal technologies began to appear enormously for processing various waste materials containing carbon in its various forms and compounds. In this article, the authors undertake a comparison of final products during the thermal pyrolytic degradation under identical conditions such as temperature, pressure, granulometry and residence time of material in rhetor. This post further explains the nature of the pyrolysis process and describes the new concept of pyrolysis technology called PYROMATIC.

Abstrakt

V poslední době se enormně začaly objevovat termické technologie na zpracování různorodých odpadních materiálu, obsahující uhlík v jeho různých formách a sloučeninách. V tomto článku se autoři zabývají srovnáním výstupních produktů při termickém pyrolyzním rozkladu za identických podmínek, jako je teplota, tlak, granulometrie a doba zdržení materiálu v retortě. Tento příspěvek dále vysvětluje podstatu pyrolýzního procesu a popisuje novou koncepci pyrolýzní technologie pod názvem PYROMATIC.

1 INTRODUCTION

VŠB - Technical University of Ostrava, together with the Arrowline a.s. and Fite a.s. companies developed and started a unique pilot plant pyrolysis technology for waste processing with performance (feat) and the possibility of winding 50 to 200 kg / h of waste material in May 2009. The pyrolysis process is the subject of constant research and development not only for the participation of universities, but also for the participation of multi-line specialized companies. PYROMATIC is a new powerful technological plant for pyrolysis processing of waste that will help reduce and energy evaluate a wide range of different materials (tires, plastics, biomass, coal, mixtures of waste, etc.) and convert them into further utilizable raw materials.

2 PYROLYSIS AND DESCRIPTION OF A PILOT PYROMATIC PLAN

2.1 Principles of pyrolysis

Pyrolysis is, together with combustion and gasification, one of the processes of thermochemical conversion. These processes are significantly different from each other in the oxygen content in the reaction area.Unlike the gasification and combustion, the pyrolysis process is used for

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the development of innovative technologies based on the decomposition of organic matter due to heat without the access of oxidizing media. In the engineering practice, this process is divided into three categories according to the temperature used, these are the low-temperature (<500 ° C), medium-temperature (500 - 800 ° C) and high-temperature processes (> 800 ° C). [1]

The thermal decomposition decreases the stability of high-molecular substances, leading to their splitting with the release of low-molecular weight substances. In essence, the thermal decomposition leads to the release of volatile matter from solid waste, which can be tires, plastics, abrasive slurries, biomass, coal, sludge from sewage treatment plants and others. [2] The thermal decomposition of the input material in the pyrolytic process generally gives rise to three main products: Carbon solid residue, liquid condensate and pyrolysis gas. These outputs from the pyrolysis technology can be used as re-feed for further processing, but mainly to produce heat and electricity [3].

2.2 Technology description of the pyrolysis unit PYROMATIC

Mechanically modified material is weighed to the desired weight and then dosed by the conveyor belt in a hermetically closed container that is purged with an inert gas to prevent oxygenates media from entering the pyrolysis process. Once the oven is warmed to the desirable temperature, the material is gradually fed into the pyrolysis retort. The minimum time for the material to stay in the pyrolysis unit is 30 minutes. Pyrolysis Retorta is heated with 5-section propane gas burners, which allow the maximum operating temperature up to 800 °C. Pyrolysed material is degraded to the solid carbon residue, which is taken into the ash box at the end of the pyrolysis, and gas phase, which is diverted from the retort pipe to the cyclone. Cyclone is a device which slows down the gas flow and with the help of gravity solid contaminating substatnces are disposed of. The purified gas is further conveyed to the primary cooling tier exchanger (pyrolysis gas - air). Secondary cooling heat exchanger consists of pyrolysis gas and water, where the gas is subcooled to stop further condensation in the piping. The condensate formed by cooling of pyrolysis gas is collected in a tank for liquid pyrolysis stage. The tank is equipped with a stirrer to avoid sedimentation of heavy hydrocarbons. The whole pyrolysis unit is controlled by the computer from the control room, which is located in the adjacent building. The outputs of sampling probes are conducted into an analyser closet where H_2, CO, CO_2, CH_4 and TOC are analysed.

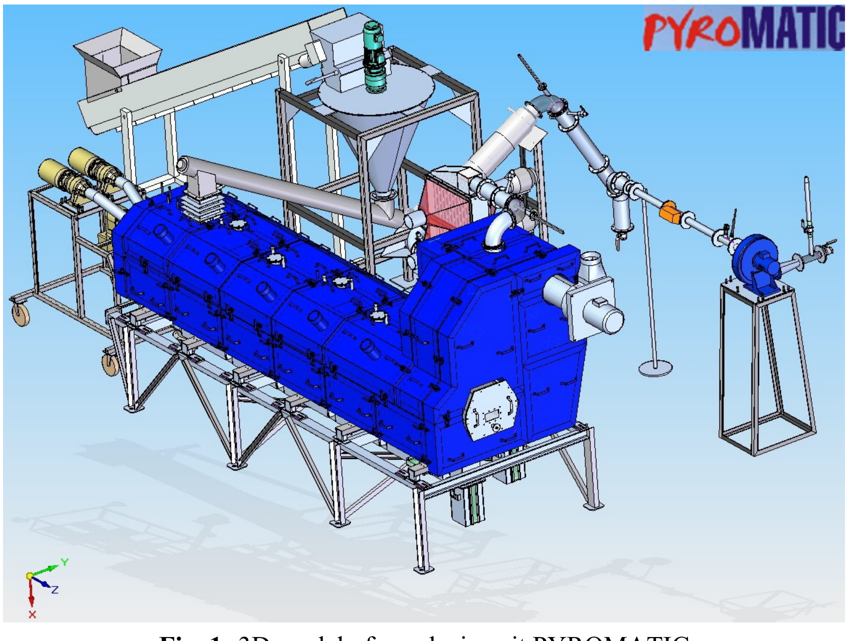


Fig. 1: 3D model of pyrolysis unit PYROMATIC

Fig. 2: Photo of pyrolysis unit PYROMATIC

3 WASTE MATERIALS, BASIC ANALYSES

3.1 Tested waste materials

The PYROMATIC VŠB -Technical University of Ostrava unit in terms of the pyrolysis process, mostly rubbery materials and waste tires have been tested. The reasons for choosing this particular type of waste as the basic input material of the pyrolysis process were following:

1. Volume of waste tires with low-life sustainability increases every year.
2. Tires are non-biodegradable, infusible and insoluble.
3. Accumulation of this type of waste causes a serious environmental problem.
4. The biggest number of tires is deposited in landfills, only 20% of the total is recycled by various techniques (such as fuel in cement kilns, as additives in asphalt used on the roads, in plants and co-combustion of coal, raw material in the rubber industry).
5. Tires have a similar chemical composition.
6. For pyrolysis tests readily available material.

3.2 Basic characteristics and analysies of waste tires

Tires have a similar chemical composition. They consist of rubber and textile and steel reinforcements. Rubber is generally composed of synthetic elastomers (poly-butadiene, styrene-butadiene, polyizopren) (27%) and natural (14%). It also contains sulfur and sulfur-containing components, carbon black, zinc oxide, hydrocarbon oils and other chemical compounds, such as stabilizers, antioxidants, etc. Tires contain 30% carbon black as a strengthening filler. Decomposition of waste tires generates creation of soot particles containing inorganic compounds [4].

Before the start of separate tests on the pyrolysis unit, the samples of tires were subjected to elemental analyses in the VŠB – TUO laboratory, which aimed at determining the usual elements, such as carbon, hydrogen, oxygen, sulfur and nitrogen. The laboratory-prepared ash from tires added data concerning the content of other elements and compounds based on the X-ray powder diffraction analysis. The sample for the analysis was not specially modified, it was only homogenized in a mortar and deposited on a glass carrier. Measurements were performed on a fully automated difractometer URD-6. The RayfleX program was used for measuring and assessing. For qualitative assessment the diffraction database PDF-2 data (version 2001) was used.

Tab. 1 Elemental composition of waste tires

Author	C (mass %)	H (mass %)	N (mass %)	S (mass %)	O (mass %)	Anorg. ash (mass%)	moisture (mass %)
VŠB-TUO	82,64	6,77	0,38	0,84	5,37	3,76	0,37
VŠB-TUO	83,78	7,09	0,24	1,23	2,17	4,78	0,62
Jong Min Lee and kol.	83,90	7,60	0,40	1,40	3,10	3,70	0,50
Gonzales and kol.	86,70	8,10	0,40	1,40	1,30	2,90	0,70

Table 1 presents analyses of elemental composition of waste tyres at VŠB-TUO and for comparison analyses published by some authors are shown. Elemental analyses show some differences, caused by the different composition of rubber and present matter. [5,6]

Tab. 2 RTG analysis – ash content of the tire

Value	Content (mass %)
ZnO – zinkit	28,13
Zn_2SiO_4 – willemit	42,20
$CaSO_4$- anhydrit	19,20
SiO_2 - cristobalit	10,41

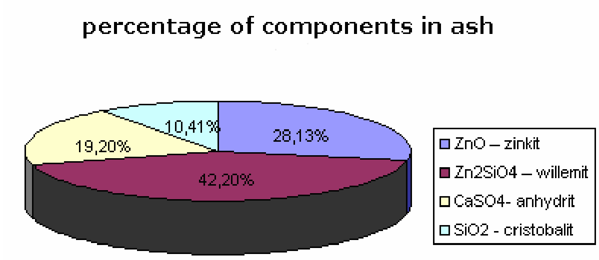


Chart 1 percentage representation of constituents in the laboratory ash

Some admixture of amorphous components can not be excluded either. Microscopic observation with a stereo microscop found that the laboratory-prepared ash is not homogeneous, but contains two morphologically and colour distinct components. They are white, mostly sharp-edged, homogeneous particles and beige-coloured irregular leaves and flakes or amorphous microparticles. It is likely that willemit is contained in card particles.

Fig. 3: Nature of the ash after burning tires

4 EVALUATION OF MATERIAL BALANCES OF FINAL PRODUCTS

The subject of pyrolysis tests was to verify the change in mass balance of waste tires at different temperatures, while other conditions were maintained. Before each attempt retorta was warmed to the desired temperature. Degradation always takes place under constant temperature.

Basic criteria and conditions of pyrolysis tests:

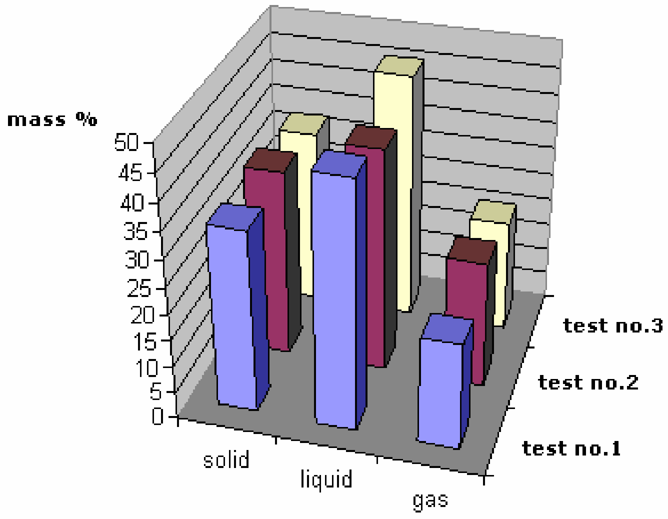
granulometry (grain size of the material) to 30 mm
moisture of the material to 20 %
input material weighed 20 kg
time for the material to stay in the rhetor 40 min
dosing screw speed 600 1/min
bulk density of tires 550 kg/m^3
maintaining vacuum in the low tens of Pascal

On the basis of our measurements the emergence of three pyrolysis products was observed, their quantity and subsequent evaluation of the mass balances.
Products of pyrolysis:

1. solid phase - pyrolysis carbon (s)
2. liquid phase - pyrolysis oil (l)
3. gaseous phase - pyrolysis gas (g)

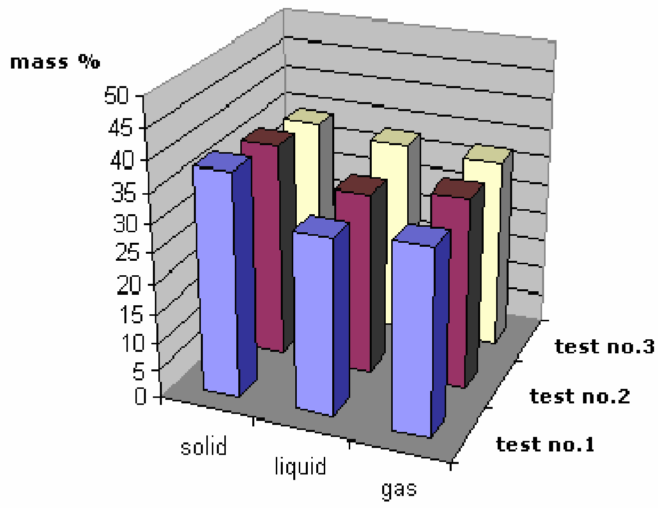
Tab. 3 Terms of pyrolysis and mass yield of fractions

Material	Weighed [kg]	Temperature [°C]	Speed [1/min]	Time delay (min)	Bulk density [kg/m^3]	s (mass %)	l (mass %)	g (mass %)
Tire	20	550	600	40	550	34,20	45,90	19,90
Tire	20	550	600	40	550	34,90	41,45	23,65
Tire	20	550	600	40	550	33,00	45,90	21,10
Tire	20	600	600	40	550	38,10	30,30	31,60
Tire	20	600	600	40	550	36,40	30,90	32,70
Tire	20	600	600	40	550	34,60	33,10	32,30
Tire	20	650	600	40	550	33,90	34,80	31,30
Tire	20	650	600	40	550	33,60	31,85	34,55
Tire	20	650	600	40	550	34,05	33,90	32,05



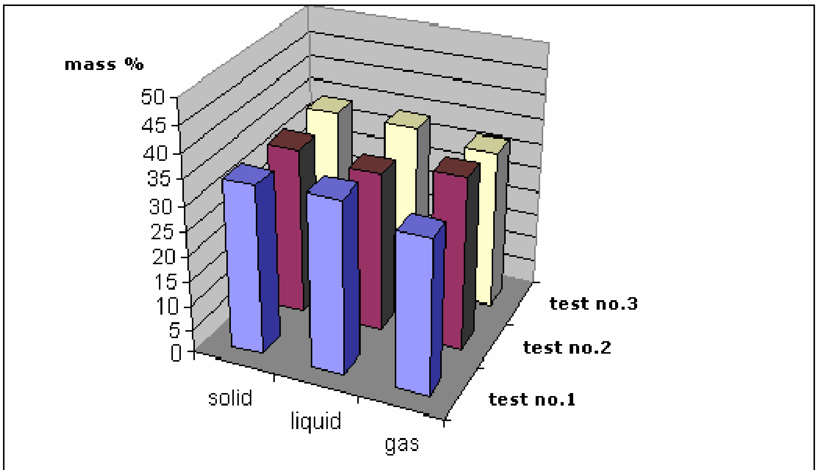
	solid	liquid	gas
test no.1	34,2 %	45,9 %	19,9 %
test no.2	34,9 %	41,45 %	23,65 %
test no.3	33 %	45,9 %	21,1 %

Chart 2 Mass balance of measurements tires at T = 550 ° C



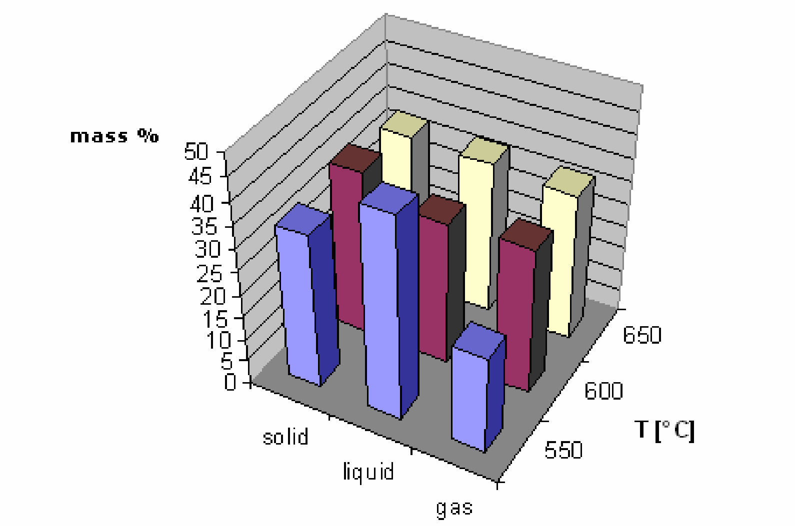
	solid	liquid	gas
test no.1	38,1 %	30,3 %	31,6 %
test no.2	36,4 %	30,9 %	32,7 %
test no.3	34,6 %	33,1 %	32,3 %

Chart 3 Mass balance of measurements tires at T = 600 ° C



	solid	liquid	gas
test no.1	33,9 %	34,8 %	31,3 %
test no.2	33,6 %	31,85 %	34,55 %
test no.3	34,05 %	33,9 %	32,05 %

Chart 4 Mass balance of measurements tires at T = 650 ° C



	solid	liquid	gas
550°C	34,03 %	44,42 %	21,55 %
600°C	36,37 %	31,43 %	32,2 %
650 °C	33,85 %	33,52 %	32,63 %

Chart 5 Summary of average values of mass balance at T = 550 ° C, 600 ° C and 650 ° C

The main parameter that influenced the yield of output products and the subsequent balance is the temperature of the pyrolysis process. The graph of measurements shows that by increasing the temperature, there was increased gas production and reduced the yield of the liquid phase in the tested waste tires.

5 CONCLUSION

The results of mass balances confirmed the assumption that increasing the temperature leads to a higher evolution of gas. The ratio between the output of the products does not only depend on the input conditions (organic/inorganic component), but depends mainly on the temperature, time delays, dose rate of the material. Given the wide range and variety of waste materials optimal pyrolysis process conditions must be chosen in order to utilize these products in the final stage in the best possible way.

Therefore, during next tests, we will focus on optimizing operating conditions, testing various waste materials (e.g. plastics, coal, biomass, sewage sludge). The main focus will continue to orientate towards the use and application of the output products in the production of electricity and heat or use in other technologies.

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