Conversion of waste rubber as an alternative route to renewable fuel production

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Abstract

Waste rubber (particularly scrap tires) generated worldwide exerts a detrimental influence on the world economy and the environment. Its fraction in municipal waste amounted to 2% by mass in 2000. By the end of 20th century, rubber production was about 34 million tons world-wide. It is estimated that 20% of tires have to be recycled every year. Dumping and land filling of used tires were the most popular methods of utilization of them until not long ago. Other alternative methods that have been used for tire recycling such as retreating, reclaiming, incineration and grinding have also significant drawbacks and/or limitations but they influence the environment to a lesser extent than dumping. Pyrolysis or gasification of waste rubber may be the best way of its utilization. The results of the thermal degradation of waste rubber performed in a new type of tubular reactor with molten metal are presented in the paper. The melting and degradation processes were carried out in an apparatus at temperatures of 390–420°C. The problems encountered with the disintegration of wastes, the heat transfer from the wall to the particles, cooking at the walls of the reactor and mixing of the molten volume of wastes are significantly reduced. Two products: gaseous (below ~ 15 weight%) and liquid (over 40 weight%) product were obtained during the degradation of waste rubber. Both streams of products were analyzed by gas chromatography. The gaseous stream contained hydrocarbons from C₂ to C₈ and the liquid product consisted of hydrocarbons C₄ to C₂₄. Over 80 mol% of liquid hydrocarbons mixture was the fraction C₄-C₁₀. The obtained liquid product may be used in petrochemical and refinery industry or may be recycled for tire manufacturing.

Keywords: thermal decomposition, waste rubber, scrap tires, molten metal.

1 Introduction

Scrap tires cause an enormous environmental and economical problem. Dumping and land filling of used tires were the worst methods of their utilization but, simultaneously, the most popular [1–5] until not a long time ago. The statistical data about the amount of waste rubber and scrap tires and the methods of their utilization are sometimes incoherent. Selected, estimated and integrated data are presented in the table 1.

Table 1: Recycling methods of scrap tires in 2004. Integrated and estimated data from different sources.

Method	UE		USA		Japan and China
	10 ⁶ Mg	%	10 ⁶ Mg	%	10 ⁶ Mg
Thermal (incineration)	0.75	30.7	1.10	43.4	Data not available
Dumping, land filling	0.95	38.9	0.87	34.3	
Civil engineering	0.28	11.5	0.29	11.4	
Direct recycling vulcanization)	0.15	6.1	0.14	5.5	
Other methods e.g. pyrolysis, cracking and chemical methods	0.31	12.7	0.14	5.3	
Total	2.44	100.0	2.54	100.0	2.2–2.6

At the end of 20th century, rubber production was about 34 million tons in the world [1–5]. A huge amount of produced rubber is used in tires production. It is estimated that 20% of tires have to be recycled every year [5]. A typical used automobile tire weighs 9–10 kg. Recoverable rubber (about 5.4–5.9 kg) consists of natural (about 35 weight%) rubber and synthetic rubber (about 65 weight%). A typical scrap truck tire weighs 18–20 kg and also contains 50–60% of recoverable rubber. The remaining part consists mainly of black carbon, zinc oxide and steel cord. These components may be also recovered.

The rubber wastes recycling industry was almost as old as the rubber production industry and over 50% of used rubber products was reclaimed in the beginning of 20th century. In 1960s and 1970s only 20% of scrap rubber was recycled and in the end of 20th century about 40–70% of used tires were dumped in massive stockpiles in many countries, which provide ideal breeding grounds for diseases and may also cause a fire hazard (e.g. in California 1999, in Poland 2003). The other alternative methods that have been used in tire recycling such as retreating, reclaiming, incineration and grinding have also significant drawbacks and/or limitations but they influence the environment to a lesser extent than dumping [1–6]. Thermal methods have been applying for rubber utilisation as well.

The thermodynamic analysis of different thermal processes points out that the best (from energy saving point of view) methods are: gasification, cracking (pyrolysis) and, finally, incineration [4]. Therefore, gasification, pyrolysis and cracking can be considered as viable recycling methods to treat the scrap tires to obtain valuable raw materials and/or energy. The scientific investigations are focused on the pyrolysis [1–3, 6, 7]. The pyrolysis gas can be used as a fuel in the pyrolysis process. A solid residue may be used for producing low-grade black carbon and the liquid product – a mixture of hydrocarbons may be used in petrochemical and refinery industry for producing fuel. Several types of reactors were invented and patented. The laboratory scale apparatus, pilot and industrial plants are generally based on tubular reactors to perform thermal pyrolysis [1–7]. Fluidized-bed reactors (for pyrolysis of disintegrated tires) have been proposed as well due to their many advantages [8–10]. However, the industrial applications of the invented reactors are rare. It means that the patented solutions are probably technically imperfect and their profitability is weak. The main weakness that should be overcome concerns the heat transfer from a heating medium to the particle of disintegrated rubber, because rubber has very low value of thermal conductivity [9, 10]. Other obstacles are connected with the utilization methods of other components of tires: black carbon, sulphur, zinc oxide and steel cord because rubber content in a tire is only about 50% by mass. Thermal conversion of rubber will be profitable only if all components of tires are recycled and the gas product of pyrolysis is desulfurized. The methods of desulfurization of gases are well known and there are also methods of utilization of black carbon [11, 12].

The problem of bad conditions of the heat transfer from a heating medium to the particle of disintegrated scrap tire may be solved by a new technology based on the thermal decomposition of waste in the molten metal bed reactor [13]. Several patents are based on this process for the degradation of organic wastes [14–17] scrap plastics. The paper presents the results of investigations on thermal rubber decomposition in molten metal.

2 Experimental work

2.1 Materials

Disintegrated waste bicycle tires and flat rubber boards were the stock for the thermal decomposition. Thirteen kilograms of alloy of tin and lead was used to create the molten metal bed. The properties of the alloy are presented in table 2.

Table 2: The composition of the alloy used in the reactor.

Fraction of tin, % weight	59–61
Fraction of lead, % weight	38–40
Fraction of impurities, % weight	1
Specific gravity, g/cm ³	8.5
Melting temperature, °C	183–185

2.2 Experimental set-up

The degradation of rubber was carried out in a new type of a tubular reactor with molten metal called “the tube in the tube”. The construction of the reactor differs from the known basin reactors that have been patented until now [14–16]. It was built from two tubes of different diameters [17]. The inner (input) tube was placed coaxially within the external (outflow) tube. A mobile piston was located inside the inner pipe for transporting wastes into the molten metal bed. The hold-up time of waste rubber in volume of the liquid metal bed depends on the piston’s speed of shifting. The scheme of the reactor and the scheme of the experimental set-up are presented in fig. 1.

(1) the reactor with a molten metal layer, (2) the loading port, (3) the piston, (4) the outlet of vapors, (5) the basic cooler of the liquid product, (6) receivers of liquid products, (7) the final cooler, (8) thermostats, (9) the computer and acquisition system data, (10) thermocouples, (11) electrical heating. A – polymers, B, C – vapor products, D – non-condensable gases to bubble flow meter and to GC, E – cooling water, F – temperature signal to the acquisition system.

(1) the external (outflow) tube, (2) the inner (input) tube, (3) the loading port, (4) the piston for wastes transporting (5) the outlet of vapors, (6) the bed of molten metal, (7),(8) thermocouples (gas phase, molten metal), (9) electrical heating.

Figure 1: The scheme of the laboratory set-up and the vertical section of the tubular reactor.

2.3 The run description

Disintegrated rubber particles were put through the loading port to the inner tube and then slowly transported by the piston into the liquid molten alloy to the end of the inner tube. Meanwhile, rubber was melted and decomposed. Products of degradation and un-decomposed components flowed out to the external tube and next to the surface of the bed. Further degradation was carried out in the

molten metal bed in the external tube and on the surface to give final products – the mixture of hydrocarbons. The vapours flowed out from the reactor were condensed in coolers. Liquid products were collected in small receivers. Gaseous product, the mixture of un-condensable hydrocarbons, flowed out from the reactor to the bubble flow meter and next through a sampling port to the ventilation system. Samples of liquid product and gaseous product were analyzed by gas chromatography. The temperatures of the molten metal bed, the gas phase and the liquid product in the coolers were measured and recorded by the acquisition data system.

3 Results and discussion

Several experiments of thermal degradation of waste rubber have been performed in the reactor with molten metal. The results of nine of them carried out in three runs are presented in the paper. The general profile and mass balances of all of them are presented in table 3. In the first run only flat rubber board was decomposed and it was performed in different way than two others. The rubber plate was cut to particles by size about $(5-15) \times (2-4) \times 3 \text{ mm}^3$. Total mass of the loaded stock was 229.5 g and it was put into the reactor in three portions of 77.00, 100.01 and 120.72 g in very short intervals, one after the other. The liquid product was received in the first cooler at the temperature 408°C of the molten metal bed 8 minutes after the time of loading. The temperature in the first, basic cooler of hydrocarbons was 23°C. The liquid product was collected into several small receivers. This enabled the liquid stream product to be calculated in time. The temperature of the gaseous phase in the reactor was between 228°C and 226°C during all the experiments. The gas product was cooled in two steps. In the first cooler, heavy hydrocarbons were condensed and then the gas flowed to the second cooler, where light condensable components were received. Non-condensable hydrocarbons flowed through the sampling port and bubble flow meter to the vent system.

Table 3: The profile and mass balance of all runs.

Run number	Mass of the stock	Temperature	Mass fraction of the products		
			gas	liquid	solid (residue)
	g	°C	% mass		
1	299.5	409–440	5.79	41.04	53.17
2A	156.97 (51.43 + 30.19 + 39.33 + 36.02)	425–427	14.74	41.28	44.4
2B		391–431			
2C		365–427			
2D		379–430			
3A	153.37 (38.02 + 38.38 + 38.39 + 38.58)	400–403	14.73	43.62	41.64
3B		403			
3C		396–403			
3D		395–403

Figure 2: The distribution of the temperature of the molten alloy in the reactor and flow rates of the gas and liquid products in the runs 1 and 3.

Runs 2 and 3 consisted of four experiments each. The stock consisted of scrap bicycle's tires. They were cut to particles of size between 5 and 10 mm. The total stock was divided in four portions, in both runs. When the liquid metal obtained demanded temperature, the first small part of disintegrated rubber particles was input through a loading port into the reactor and then transported into molten metal by the piston. The gaseous product was obtained in a few minutes after loading and in further few minutes the liquid product was collected to only one collector for each experiment (each decomposed portion of rubber). When the flow of product was decreased, the temperature of the molten metal bed was changed. When new conditions were achieved another part of rubber waste was loaded to the reactor for the next experiment.

The profile of product flow rates, the temperature distribution of molten metal for the run 1 and 3 is presented in fig. 2, as a representative example.

Figure 3: The carbon number gas product (a) and liquid product distribution for rubber decomposition in the run 3.

Runs 2 and 3 were very similar. The method of performing the runs and the amount of the stock material were almost the same. The liquid and gas product distributions for run 4 are presented in fig. 3. It is also representative of all experiments. The compositions of the gas and liquid samples were similar and stable during all runs as it can be seen in fig. 3. The lines present the GC analysis results of different samples collected with the time. Run 1 was carried out in another way and under other conditions than those of runs 2 and 3 but the average liquid products obtained from all experiments are very similar and stable for all runs as shown in fig. 4. The fraction compositions of average liquid samples collected in all runs are presented in table 4. The liquid products obtained from thermal decomposition of waste rubber in the molten metal contained above 95% mol most valuable, light fractions of hydrocarbons (called “gasoline” (C_4 - C_{10}) and “diesel” (C_{11} - C_{16}) fraction. The composition of the liquid product makes it usable as a stock in petrochemical or rubber industry.

Figure 4: The carbon number average liquid product distribution for rubber decomposition in the runs: 1, 2 and 3.

Table 4: Fraction composition of the average liquid products.

Run number		1	2 (A-D)	3 (A-D)
Fraction		Fraction composition of the liquid product		
C ₄ -C ₁₀	% mol	68.8	75.3-75.8	73.6-77.7
C ₁₁ -C ₁₆	% mol	24.2	21.2-22.0	19.6-24.2
C ₁₇ -C ₂₄	%mol	7.0	2.6-2.9	2.0-3.0
paraffin	% mol	31.5	27.5-32.3	38.5-39.7
olefins	%mol	68.5	65.7-72.6	60.3-62.5

The received products are generally the mixture of paraffin and olefins. The ratio of paraffin to olefins is presented in table 4 too for liquid products. The amount of olefins is about 50% greater than that of paraffin. The liquid products are fluids in ambient conditions; however, black carbon is suspended in a liquid mixture. Therefore, before further use, it has to be clarified.

The qualitative analysis of the liquid samples made by FTIR proved that the content of aromatic hydrocarbons was below 5 mol.%.

The content of heavy metals in liquid product was analyzed too and it was made by AAS. The concentration (in liquid) of lead (Pb) and tin (Sn) was between 20 and 30 mg/kg, of zinc below 17 mg/kg, of nickel (Ni) and chromium (Cr) below 1.5 mg/kg. The relative analytical errors of metals determination were: 0.8–1.0% (for Pb, Sn, Zn) and 4% (for Ni and Cr).

4 Conclusions

The thermal decomposition of rubber wastes performed in a reactor with molten metal may have many advantages. The process is fast. The problems with the heat transfer resistance between the particles of wastes and the heating medium is overcome due to direct contact between rubber and molten metal. Therefore, the cooking processes may be minimized. The ratio of the amount of gaseous product to the amount of liquid product is less than that resulting from other thermal decomposition processes. The liquid product contains mainly gasoline fraction of hydrocarbons. The hold-up time of wastes in the reactor and the reaction time are shorter than in classical reactors applied for rubber pyrolysis. Therefore the amount of the recombination reactions products is minimized and the fraction of aromatic hydrocarbons is smaller than in other processes based on pyrolysis in tubular or fluidized reactors. The content of heavy metals is small that means that the process temperature is proper and the metal particles and metal ions have not been transferred to the liquid products. However, thermal cracking processes of rubber in the reactor with molten metal bed (as other thermal processes) will be cost-effective if all of the obtained products: not only hydrocarbons but, for example, black carbon as well may be recycled and used for producing fuel and other useful semi-products. About 10% of recovered energy has to be used (recycled) for the disintegration of waste rubber.

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