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Research Article

Improved demineralization of the carbon black obtained from the pyrolysis of the sidewall and tread of scrap Tires: Extraction of some micro-/macro-nutrient elements of plants

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ABSTRACT

In parallel with the increasing tyre production in the world, the amount of scrap tyres is also increasing. Within the scope of scrap tyre management, studies aimed at preventing the accumulation of tyres that threaten the world in terms of human health and the environment can be briefly defined as 4RL, including recycling, reuse, recovery, regeneration, landfill. Current methods have not yet completely controlled the accumulation of scrap tires. In this study, sidewall and tread parts of scrap tires with different compositions were pyrolyzed separately. Pyrolytic carbon black has been upgraded with an improved acid-base extraction method. Two different carbon blacks of high commercial value were obtained from the tire sidewall and tread. Since the mixture obtained from acidic-basic extraction, consisting of elements such as Zn, K, Na, Ca and S, are micro and macro nutrients of plants, the solution can be used directly in the fertilizer industry. With this study, the commercial value of solid residue, which is a major bottleneck in tire pyrolysis plants, has been increased. The pyrolysis method has been transformed into a more feasible project.

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INTRODUCTION

The amount of scrap tyres is increasing day by day with the increase in passenger vehicles, public transportation vehicles, and construction machines around the world. More than 1.5 billion tons of tyre scrap is generated every year. Tyre scraps left in the environment fall into the group of hazardous waste and remain without self-degradation due to its chemical structure consisting of strong polymeric crosslinks [1]. The rainwater accumulated in the scrap tyres thrown into the environment or stored regularly becomes the habitat of mosquitoes and parasites, which poses a great threat to living things as it causes the spread of epidemics. The flammability of tyres collected in landfills is very high and the fires cause great environmental pollution [2]. In the USA, a fire in a tyre storage area lasted about 9 months [3]. Scrap tyre management around the world has become important to minimize these threats. The methods of combating scrap tyres, which seriously threaten life, are generally grouped under five headings as reduction, reuse, recycling, recovery, and reclamation, and it would not be wrong to call these studies 4RL.

Obtaining pyrolytic fuel (energy) and pyrolytic carbon black (polymer filler and dye) from the pyrolysis of scrap tires is one of the most important methods in waste tire manage-

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ment [4–8]. The process of converting hydrocarbons into smaller molecules by thermal cracking in oxygen-free conditions at high temperatures is called pyrolysis [7–10]. Carbon black (CB) and polymer (rubber) are the main components of the tyre body. The pyrolytic carbon black (CB_p) and pyrolytic oil (liquid fuel) are the two major products of tire pyrolysis [9]. World carbon black production is around 14 million metric tons according to 2020 data [10]. The carbon black is the most important filler and dyestuff used in the tyre and polymer industry. In tire manufacturing, 20–30% CB is added to the rubber [1]. Depending on tire types and pyrolysis conditions, between 30% and 40% CB_p is obtained from the pyrolysis of scrap tires [1, 6]. The two major components of ash in carbon black are SiO_2 and Zn (zinc oxide, zinc sulfide). Industrial use of CB_p is difficult due to the high ash content. To date, some acid-base leaching methods with mineral acids (HCl, H_2SO_4, HNO_3, HF) and NaOH have been studied to reduce the ash amount of CB_p [1, 11, 12]. In metal and sulfur extraction, the highest efficiency was obtained in two-stage acidic demineralization studies (mineral acid and HF) [11]. However, due to the difficulty of application and high cost of toxic HF, it has not become popular in industrial applications. Mineral acid-NaOH methods could not achieve as much success as HF because the interaction between CB_p and the extraction solution was not strong. There is still a need for continued research on upgrading CB_p.

Seventeen elements in soil are important nutrients for plants [13]. Among these, macro-nutrient elements are N, P, K, Ca, Mg and S, and micro-nutrient are Fe, Zn, Cu, B, Mn, Mo, Cl and others [13]. It is known that Zn, which is one of the two major components of ash in CB_p, shows important activity in plant development [14–16]. These elements are the cornerstones of many biological reactions that are vital in plant metabolism, such as enzymes and the formation of amino acids. The ash composition in CB_p consists of micro-nutrients and macro-nutrients such as Zn, Ca, K, Fe and S.

In this study, solid-liquid extraction efficiency was increased by adding dispersive, wetting and complexing agents to the know acid-base extraction method in CB_p demineralization studies. It was determined that the elements in the extract constitute micro-nutrients and macro-nutrients that are vital for plants. Thus, CB_p obtained from pyrolysis of tire, which has a very low market value and constitutes a serious bottleneck for the pyrolysis method, has been converted into carbon black with high commercial value, and an important raw material source for the fertilizer industry has been obtained as a by-product of extraction method. Recycling scrap tires using the pyrolysis method has become a more feasible project.

EXPERIMENTAL

The pyrolysis processes were carried out in a mechanism consisting of heating the shredded tyres in a fixed bad reactor, gas-liquid separation by cooling in a condenser, and cleaning (desulfurization) of non-condensed gases. In the heating process, a fixed bad reactor made of 2 mm stainless steel, 100 mm in diameter, 200 mm in height, heated with a 4 kW electrical resistance was used. The reactor was isolated by wrapping it with silica wool. Temperature and pressure in the reactor were controlled by PID. A straight tube bundle condenser with a length of 700 mm and a diameter of 100 mm was used to separate the pyrolytic gases. The non-condensed gases were desulfurized by passing through a container with a basic solution and burned with a burner flame. The pyrolysis processes were carried out at atmospheric pressure. Leco, CHNS-932 elemental analyzer was used for C, H, N, S analysis in carbon black. Carbon black surface area was measured with the Gemini VII 2390 series from Micromeritics. The metal composition of the ash was determined with a 50 kV, 500 µA, Malvern Pananalytical Epsilon 1 X-ray fluorescence spectrometer (XRF). In the carbon black refining process, a blanket-wrapped Dissolver Dispermat® LC55 dispersive mixing device heated with a 2 kW resistance was used. Binder FP 720 model oven was used for drying operations, Microtest MKF-7 model muffle furnace was used for high-temperature heating. Scrap tyres were obtained from tyre changing services. The sidewall and back parts of the tyres were separated with chisel blades and sliced in 1–2 cm sizes. It was then washed with water and acetone and dried at room temperature. Elemental analyzes of the selected tyres are given in Table 1.

Table 1. Sidewall and tread compositions of tyres used in research

Component	Sidewall	Tread
Ultimate analysis, %		
C	81.67	74.93
H	7.74	6.59
N	0.41	0.26
O	2.68	1.89
S	1.22	0.76
Proximate analysis, %		
Moisture (M)	1.46	3.25
Volatile matter (VM)	66.23	61.88
Ash (A)	6.28	15.57
Fixed carbon (FC)	26.03	19.30
Zn	2.68	2.36

Pyrolysis

The tyre sidewall and tread pieces, which were previously sliced in 1–2 cm sizes, were weighed separately 800 g and filled into the pyrolysis reactor, heated at 5 °C/min, and the pyrolysis process was carried out at 450, 500, 550, 600 °C temperatures for 4 hours. Pyrolytic gases were condensed and accumulated in the liquid collection container, and non-condensed gases were passed through a 4 M NaOH solution and burned in the burner. The reactor cover, which was cooled to room temperature, was opened and all carbon black was discharged. Metallic impurities in carbon black were separated by a water trap and magnet.

Demineralization of CB_p

Metal extraction from pyrolytic carbon black consists of acidic and basic ash removal steps. In acidic ash removal (deashing) process, zinc metal is extracted by treating pyrolytic carbon black with acid solution, dispersing agent and complexing agent, and acidic washing precipitate is obtained by washing the solid phase. In the basic ash removal process, the acidic precipitate is treated with a basic solution and an oxidizing agent to extract the silicon component, the solid phase is filtered, washed and dried.

The Acidic Deashing

A mixture of 10 g of carbon black, 100 ml of HCl, 10 ml of ethyl alcohol (EA) as a dispersing agent and 0,5 g of citric acid (CA) as a complexing agent is mechanically mixed at 50 °C until it becomes a homogeneous solution. Then it is mixed for another 2 hours with a 40 kHz ultrasonic mixer. The solution is filtered and the precipitate is washed until pH=7. The zinc rich aqueous phase is zinc extraction solution.

The Basic Deashing

A solution of 5 g of CB_p, 4.10^{-3} wt.% of potassium ferrate, 5 M NaOH in 50 mL of water is heated up to 85 °C with mechanical mixing until a homogeneous solution is obtained. Next, the mixture was stirred for 1 hour with a 40 kHz ultrasonic stirrer at 85 °C, 300 rpm. 25 mL of 30% sodium hypochlorite was added to the mixture twice with one hour intervals and mixed for 2 more hours. Then it was cooled to room temperature, centrifuged at 5000 rpm, washed until pH=7 and filtered. The precipitate dried in an oven at 120 °C is refined carbon black.

RESULTS AND DISCUSSION

In the thermochemical cracking reaction of scrap tires, volatile compounds and carbonaceous residue are formed. Most of the volatile components are condensed to obtain pyrolytic oil. Non-condensed gases consisting of C1–C4 hydrocarbons are considered gas-fuel since they have high calorific value. At the end of pyrolysis, carbon black, silica, zinc, other minerals and sulfur compounds added in the manufacture of the tire are obtained as solid residue and are also called pyrolytic carbon black (CB_p) [6].

Carbon black, used as one of the main components in tire manufacturing, is classified by ASTM with various codes between N100-N900, depending on parameters such as size, surface area, pore diameter and surface activity [17]. N refers to the normal carbonation rate, and numbers refer to grain size. Carbon blacks with small particle sizes have a microporous structure and are highly structured. The dispersion of high-structure CB in the polymer is more difficult than low-structure CB, but the dyeing intensity is stronger [17]. Although low-structure carbon blacks are better dispersed in the polymer, they reduce the mechanical strength of the polymer. In the interactions between the polymer and carbon black, alcoholic, carboxylic acid, carboxylic anhydride, lactone, lactols, phenol, and hydroxyl groups on the surface of carbon black play an important role in surface activity [18, 19]. Some changes occur in the surface morphology of carbon black due to the volacanization reactions of rubber and thermochemical reactions during high temperature pyrolysis [18, 19]. Substances formed during the vulcanization reactions that occur between CB and rubber molecules, S and inorganic substances fill the pores of carbon black. Additionally, some functional groups may be deactivated due to reactions between the functional groups on the CB_p surface with rubber molecules and sulfur. Carbonaceous residues formed by repolymerization and dealkylation reactions occurring in the gas phase during pyrolysis refill the CB_p pores in the form of coked deposits [18, 19]. The physicochemical properties of CB_p differ from commercial carbon blacks due to changes in the pore diameter and surface activity of CB_p, as well as the masking of the surface activity by carbonaceous residues. Another reason why CB_p does not have a specific standard is that different types of carbon black and silica combinations are used in the sidewall and tread during tire manufacturing [20, 21]. High-structure carbon blacks with a large surface area, which provide high wear and friction resistance even at low temperatures, are preferred in the tire tread. Carbon blacks, which provide high strength and flex resistance and are easily dispersed in polymer, are preferred on the sidewall. Since carbon blacks such as N110, which have high structure and large surface area, are difficult to disperse in the polymer, they are not preferred to be used in tire manufacturing. Recently, carbon blacks and inorganic additives such as SiO_2 and $CaCO_3$ have begun to be used in tire manufacturing as hybrid fillers [20, 21]. For example, in Toyoya Car Corp.'s patented work, the use of a hybrid filler consisting of Seast 3 coded carbon black (equivalent to N330) and silica in the manufacture of the tire sidewall is described. In the patented work of Sumitomo Rubber Industries Ltd, N359 carbon black and silica hybrid filler was used in the tire tread [20, 21]. As a general approach, it can be said that high-structure carbon blacks with mesopore diameter are used instead of low-structure carbon blacks, which have high porosity and weaken the wear resistance of the polymer, in the tire tread and sidewall. Additionally, it seems impossible to define a specific standard quality for revovered carbon black, as different types of carbon black are used in different tire types and tire parts, depending on tire manufacturers' formulations.

In this study, the tire tread and sidewall parts were pyrolyzed separately to separate the two different types of carbon black used in the tire tread and sidewall parts. Since the main subject of the study was the removal of inorganic components in carbon black, no catalyst was used to change the mineral composition of the ash, and parameters that would affect the pyrolysis efficiency such as heating rate and tire size were not examined. Regardless of the brand of tyre types, sidewall and tread tyres were separated and cut into 1–2 cm sizes with the help of chisels. Sidewall and tread tyres have been pyrolyzed separately between 450 °C and 600 °C. Product yields depending on the temperature in the pyrolysis process are given in Table 2. Maximum pyrolytic oil was obtained as 49.76 wt.% from the tire tread and 51.26 wt.% from the tire sidewall at 550 °C. The highest

Table 2. The proportions of tread and sidewall pyrolysis products at different temperatures

T, °C	Tread/%			Side wall/%		
	CB_p	Oil	Gas	CB_p	Oil	Gas
450	41.5	44.74	13.76	39.12	47.21	13.67
500	39.42	45.62	14.96	37.43	47.62	14.95
550	38.53	49.76	11.71	36.22	51.26	12.52
600	36.34	48.51	15.15	34.16	49.74	16.1

Table 3. The pyrolytic carbon black composition obtained from sidewall and tread tyres depending on the pyrolysis temperature

	Ultimate analysis (wt.%)					Proximate analysis (wt.%)			
T, °C	C	H	N	O	S	A	M	VM	FC
Side wall									
450	80.86	1.58	0.59	3.95	1.63	12.28	1.66	7.45	78.61
500	84.92	1.65	0.43	3.79	1.69	10.52	0.86	4.77	83.85
550	86.41	1.73	0.52	3.21	1.2	9.82	0.82	4.57	84.79
600	87.16	1.78	0.56	3.39	1.66	9.12	0.87	4.32	85.69
Tread									
450	49.12	1.63	0.55	2.68	2.48	49.41	2.97	8.67	38.95
500	54.23	1.54	0.41	2.47	2.13	46.23	2.68	4.98	46.11
550	56.92	1.48	0.43	2.51	1.86	44.89	2.41	4.82	47.88
600	57.16	1.45	0.49	2.18	1.98	44.18	2.18	4.58	49.06

A: Ash; M: Moisture; VM: Volatile matter; FC: Fixed carbon.

amount of carbon black was obtained at 450 °C, 41.5 wt.% and 39.12 wt.% for the tire tread and sidewall, respectively. There was no significant increase in the amount of CB_p and oil after 550 °C. The high amount of CB_p at 450 °C show that the hydrocarbons in the carbon black matrix are not completely cracked, the carbon-like deposit formed by secondary reactions between gas molecules covers the carbon black surface, and pyrolysis is not completed. Moulin et al. [22], as seen in Figure 1, stated that in the dTG and TG diagram obtained from termogravimetric analyzes of the tire up to 800 °C, thermal degradation started at 150 °C, and mass loss began to be observed around 300 °C due to the degradation of additives such as process oils and plasticizers. They showed in dTG curves that most of the rubber decomposes between 350 °C and 500 °C, and mass loss is completed at 550 °C.

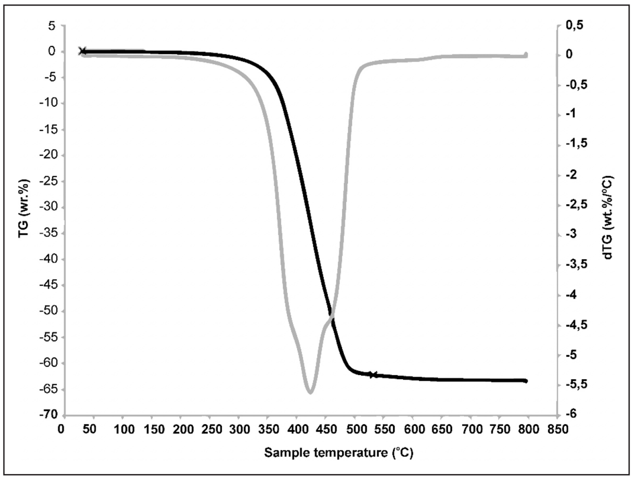

Figure 1. TGA-DTA analysis on the tire sample at 5 °C/min heating rate [22].

In the pyrolysis experiments carried out by Yazdani et al. [23] between 400 °C–600 °C, distinct peaks were observed in the range of 660–3000 cm^{-1} from the FT-IR analyzes of the pyrolytic oil. They determined that the 3050 cm^{-1} band of C-H strench indicates the aromatic structure and shows the highest value at 500 °C and 550 °C. Researchers stated that pyrolysis was completed at 550 °C [23]. In the experiments conducted with tire tread and sidewalls, the maximum pyrolytic oil yield was obtained at 550 °C, which coincides with both literature studies [22, 23]. It has been understood that in order to complete the thermal pyrolysis of scrap tires, the temperature must be exceeded 500 °C, and since there is no change in the yield of the products after 550 °C, the pyrolysis temperature must be between 500 °C and 550 °C.

Ultimate and proximate analyzes of CB_p obtained at different temperatures are given in Table 3. As seen in Table 3, the amount of volatile matter (VM) of carbon blacks obtained from the tire sidewall and tread between 450 °C and 600 °C varies in the range of 7.45 wt%–4.32 wt% and 8.67 wt%–4.58 wt%, respectively. At low temperature, the VM value was found to be higher than the sidewall due to the presence of

Table 4. Analysis results of demineralized pyrolytic carbon black at 550 °C

Samples	Sidewall	Tread	N234	N330	N339	N550
C	94.29	94.33	95.2	96	97.79	98.7
H	0.50	0.60				
N	0.34	0.48				
O	3.66	3.50				
S	0.80	0.73				
Ash	0.41	0.36				
M	0.53	0.60				
VM	3.40	3.82				
FC	94.38	94.46				
SA, m^2/g	76.82	99.76	126	83	96	42
Iodine number, mg/g	77.40	84.43	120	82	93	43
DB_p, $cm^3/100$ g	98.12	101.50	125	102	115	121

DPPA: Dibutylphtalate adsorption; M: Moisture; VM: Volatile matter; FC: Fixed carbon.

more carbonaceous deposits on the carbon black surface obtained from the tire tread. At high temperatures, the amount of VM for both CB_p was found to be close to each other.

Table 3 shows that the ash values for the tire tread are almost four times higher than those for the sidewall. One of the reasons for this is that due to the larger pore diameter of the carbon black used in the tire tread, more coked carbon residues and mineral matter cover the carbon black surface and fill its pores. The other main reason is the use of high amounts of silica as a filler along with carbon black in the tire tread. As a result, the FC values of the carbon blacks obtained from the tire tread were found to be much lower than those from the tire sidewall. From these data, it is understood that the carbon black used in the tire tread has a larger pore diameter and lower structure than the tire sidewall. FC values increased due to the decrease in the amount of volatile matter with the increase in temperature. Since carbonaceous residues containing polymer molecules cross-linked with sulfur and ZnS, which is formed as a result of the reaction of S and Zn, are more in the tread part, the sulfur value is higher than in the sidewall part. In Figure 2, Mis-Fernandez et al. [24], from X-Ray Diffraction analysis of tire pyrolysis between 450–750 °C, show that characteristic peaks of ZnO are very strong at 450 °C, characteristic peaks of ZnS begin to appear after 550 °C, and ZnS peaks are very strong at 750 °C. They stated that after 750 °C, almost all Zn reacted with S to form ZnS.

The amount of iodine adsorption (iodine number) and N_2 adsorption provide important information about the surface area and pore structure of carbon black [1, 25]. Although the iodine number is found to be slightly different from the surface area determined according to N_2 adsorption due to the interaction of iodine with carbonaceous residues on the surface, the difference gives an idea about the carbonaceous residue and mineral substance covering the pore structure. An important parameter that determines the quality of carbon black is the size of the branched chains in carbon black aggregates, which can be determined by di-butyl phthalate adsorption (DBP) [1, 25]. As seen in Table 4, in demineralized CB_p obtained from the tire tread, although the analysis results were slightly different from N339 due to the carbonaceous residues and inorganic substances weakening the formation of a great, the values were found closer to N339. It is desirable to use high-structure, microporous carbon blacks in the tire tread, which improve the friction and wear resistance of the polymer. However, from the iodine number, N_2 adsorption and DBP adsorption data, it was understood that carbon black with a lower structure was used from the sidewall (similar to N330). The possible reason for this may be that since high-structure microporous carbon blacks are difficult to disperse in rubber, mesoporous carbon blacks, which are more easily dispersed, have been adopted to increase the wear and friction

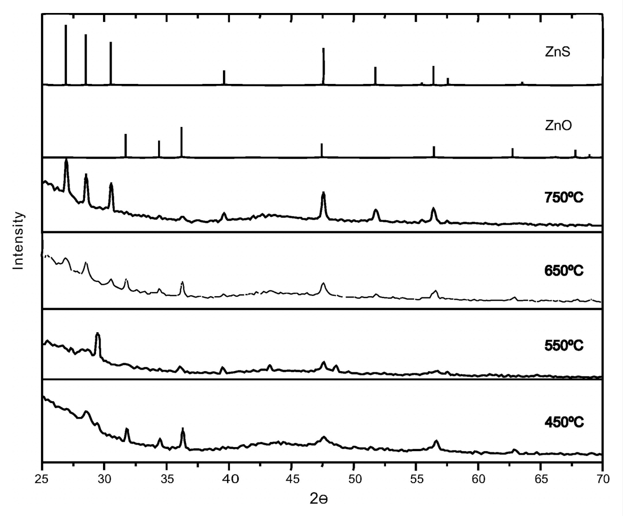

Figure 2. X-ray diffraction for pyrolytic process from 450 °C to 750 °C [24].

Table 5. Elemental analysis results of CB_p from acidic and basic deashing steps at 550 °C

Samples	Sidewall				Tread			
	CB_p wt. %	HCl wt. %	HCl+CA+EA wt. %	NaOH+Oxidant wt. %	CB_p wt. %	HCl wt. %	HCl+CA+EA wt. %	NaOH+Oxidant wt. %
Si	17,23	65,22	74,20	1,18	40,68	63,63	70,87	1,96
Zn	47,36	6,96	3,76	0,74	20,66	5,50	3,73	0,44
K	1,07	1,14	0,90	n.r.	1,13	1,21	1,03	n.r.
Na	1,01	1,16	0,80	n.r.	1,10	1,18	0,75	n.r.
Al	3,45	1,79	0,14	n.r.	3,09	1,69	0,13	n.r.
Fe	3,23	1,07	0,12	n.r.	3,32	1,11	0,11	n.r.
Mg	1,28	1,06	0,18	n.r.	1,54	1,36	0,16	n.r.
Ca	5,63	1,86	0,15	n.r.	5,38	1,23	0,13	n.r.

n.r.: Note reported under 0,1 wt. %.

resistance with silica reinforcement. The negative effects of mesoporous carbon blacks producing larger aggregations were eliminated with silica. It can be said that, not being a general rule, low-structure, high-pore diameter carbon blacks such as N550 or N660 were not used on the sidewall and tread of the tire sample studied.

In Table 4, it is observed that the sulfur value also decreased significantly. It has been observed that sulfur in the form of metal sulfides is successfully reduced in the two-stage extraction method with the addition of complexing agents and oxidants.

Demineralization of CB_p consists of a two-stage solid-liquid extraction (acid-base extraction) method. The method is also known as leaching. CB_p was first treated with HCl, then the acid step was repeated by adding ethyl alcohol as a surface wetting and dispersing agent and citric acid as a complexing agent to the acid solution. In the continuation of the study, the acid-treated CB_p was treated with NaOH solution containing oxidant substances to extract silica, sulfur and other metals. In Table 5, the extraction results of single-stage HCl extraction, HCl extraction with CA and EA addition, and NaOH extraction with oxidant addition are given.

Acidic Extraction: The following reactions occur between HCl and the major metallic components in CB_p.

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \quad (1)$$

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O \quad (2)$$

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O \quad (3)$$

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O \quad (4)$$

As seen from Eq (1), 2 mol of HCl is required for every 1 mol of ZnO. Since ZnO is 81.40 g/mol, theoritically 89,68 g of HCl is required stoichiometrically for every 100 grams of zinc oxide. The amount of zinc in CB_p obtained from tire sidewall and tread regions at 550 °C, are 47.36% and 20.66%, respectively. Theoretically, 52.18 g HCl and 22.76 g of HCl are required for tread and sidewall CB_p, respectively. An acid solution 10 times the weight of CB_p was used in the experiments. Considering the other elements in the carbon surface matrix, the use of 4 M HCl is also compatible with literature information [1, 15, 16].

As seen in Table 5, zinc extraction efficiency is low without the use of surface wetting EA and complexing CA. Depending on the metal extraction amount of HCl, the SiO_2 ratio in CB_p increased. The addition of surface wetting EA increased the hydrophilicity of metals, and CA not only gave more protonium ions to the solution, but also significantly increased the extraction efficiency by complexing with metals. After the acidic stage, silica concentration increases due to the extraction of other metals.

Basic Extraction: The reaction between ZnS, SiO_2 with NaOH is as follows.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (5)$$

$$ZnS + 2NaOH \rightarrow Na_2S + Zn(OH)_2 \quad (6)$$

Since $Zn(OH)_2$ has low solubility in water, it passes into the aqueous phase during neutralization of the solid phase with sulfuric acid, as seen in Eq. 7.

$$H_2SO_4 + Zn(OH)_2 \rightarrow ZnSO_4 + 2H_2O \quad (7)$$

After acidic metal extraction experiments in the range of 450 °C–600 °C, remaining SiO_2 for the tire sidewall and tread are 74.20 wt.% and 70.87 wt%, respectively. The amount of Zn is 3.76 wt.% and wt. 3.73 wt.%, respectively. Theoretically, 102.50 g and 98.03 g of NaOH are required to remove Zn and Si from every 100 g of sidewall and tread carbon black after the acidic deashing stage. 2.56 M and 2.45 M NaOH were calculated for each 100 g of sidewall and tread carbon black, respectively. It was taken into account that more base should be used due to the steric hindrance of other metals in CB_p and carbonaceous residues of the CB_p surface matrix, and 5 M NaOH was used in accordance with the literature [1, 5, 16]. As seen in Table 5, the amount of Si in the sidewall and tread decreased from 17.23 wt.% to 1.18 wt.% and from 40.68 wt.% to 1.96 wt.%, respectively.

As seen in Table 5, potassium ferrate and hypochlorite added in the basic extraction stage, zinc, silica and calcium, which are the major components of carbon black, were ex-

Table 6. Amounts of inorganic elements extracted from CB$_p$ at 550 °C

	Sidewall			Tread		
Sample	**Wt.% in ash**	**Recovery, wt. %**	**Extraction, g/L**	**Wt. % in ash**	**Recovery, wt.%**	**Extraction, g/L**
Si	17.23	16.05	1.51	40.68	38.72	13.50
Zn	47.36	46.62	4.40	20.66	20.22	7.05
K	1.07	1.07	0.10	1.13	1.13	0.40
Na	1.01	1.01	0.10	1.10	1.10	0.39
Al	3.45	3.45	0.33	3.09	3.09	1.08
Fe	3.23	3.23	0.30	3.32	3.32	1.16
Mg	1.28	1.28	0.12	1.54	1.54	0.54
Ca	5.63	5.63	0.53	5.38	5.38	1.88

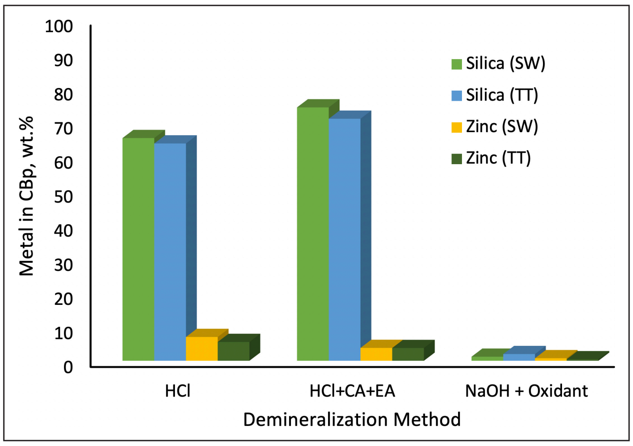

Figure 3. Zn and Si in CBP as a result of acidic and basic deashing steps at 550 °C.

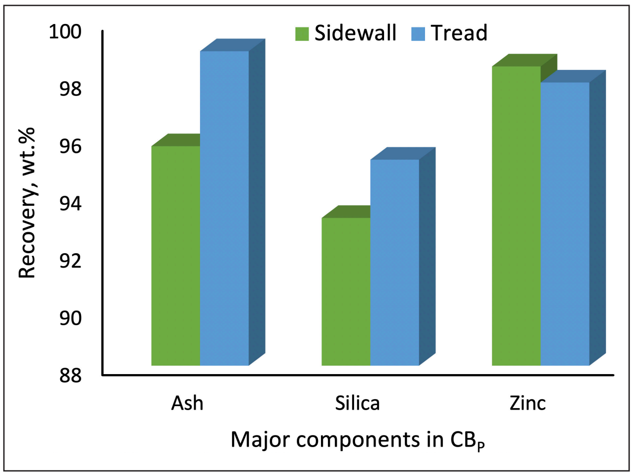

Figure 4. Deminerlization results of CBP at 550 °C.

tracted with great efficiency in the basic stage. Components above 1 wt.% are given in Table 5. As seen in Figure 3, silica could not be extracted alone in the acid phase, zinc was largely removed, and all minerals were extracted with great efficiency in the basic phase.

Although SiO$_2$ is the main component of the hybrid filler, it reduces the staining intensity of CB$_p$ because it changes the pore diameter and surface activity of carbon black. Additionally, SiO$_2$, which has a hydrophilic surface, reduces the dispersion of carbon black in the hydrophobic polymer matrix. SiO$_2$ decomposes as a commercially valuable by-product in the form of Na$_2$SiO$_3$ (water-glass) as a result of a basic reaction.

Sodium hypochlorite ionization reaction is given in Eq. 8 and Eq. 9. It is unstable at low pH values. Stable at pH>10 with addition of NaOH [26].

$$HClO \rightarrow H^+ + ClO^- \qquad K = 3.3 \times 10^{-8} \tag{8}$$

$$HClO + Cl^- + H^+ \rightarrow Cl_2 + H_2O \qquad K = 2.3 \times 10^3 \tag{9}$$

Sulfonyl compounds are formed as a result of reactions between sulfur compounds in the form of sulfide or disulfide in the hydrocarbon structure and hypochlorite. The sulfonyl then oxidizes into sulfonate or sulfate.

$$R - S - R' + 2ClO^- \rightarrow RSClO^- + R'ClO^- \tag{10}$$

$$RS - S - R' + 2ClO^- \rightarrow RSClO^- + R'SClO^- \tag{11}$$

$$RSClO^- + 2H_2O \rightarrow RSO_3H + 3H^+ + Cl^- + 3e \tag{12}$$

$$RSClO^- + 3H_2O \rightarrow RCl + 6H^+ + SO_4^{2-} + 5e \tag{13}$$

The reaction between metallic compounds of sulfur, for example ZnS, and hypochlorite is given in Eq. (14).

$$ZnS + 4ClO^- + 2H_2O \rightarrow Zn(OH)_2 + 4Cl^- + SO_4^{2-} + 2H^+ \tag{14}$$

As can be clearly seen from Table 5, after the demineralization studies of the sidewall and tread carbon blacks, the sulfur value decreased from 1.2 wt.% to 0.8 wt.% and from 1.86 wt.% to 0.73 wt.%. has decreased. CA and EA added in the acidic stage and hypochlorite added in the basic stage made a great contribution to the desulfurization of CB$_p$. As seen in Figure 4, the amount of zinc recovery is higher in the tire sidewall. Silica and ash removal is greater on the tread.

Micro-Nutrients and Macro-Nutrients of Plants

Zinc is an important component of various enzymes that drive metabolic reactions in plants. These enzymes in the plant tissue contribute to the growth and development of the plant. Zinc deficiency causes a decrease in the formation of carbohydrates, proteins, and chlorophyll in plants.

Zinc is an important plant micronutrient that strengthens roots and leaves in fertilizers. Fertilizers containing zinc, which is a very important nutrient source for plants, especially in barren soils with high lime content, cannot be used as widely as desired due to the high cost of zinc. Efforts to reduce the cost of zinc-containing fertilizers will increase the use of such fertilizers in a wider area [14]. As seen in Table 6, K and Ca minerals, which are macro-nutrient elements of plants, are also included in carbon black ash. Micro and macro-nutrient elements in the solution obtained from pyrolytic carbon black are given in Table 6.

CB_p obtained from tire sidewall and tread was treated with 10 times solution in acidic and basic levels, and the amount of mimeral substance extracted for 100 g CB_p is given in g/L. Solutions can be used directly as stock material in fertilizer formulations containing micro and macro nutrients, their concentration can be increased by evaporation-crystallization, or they can be obtained as pure components by electrochemical methods. For example, as a result of the mineral recovery of 1 ton of CB_p, extract containing 40.40 kg and 70.50 kg of zinc is obtained from the sidewall and tread parts, respectively. 1 ton of solution prepared with a 1:1 mixture of extracts yields 57.05 kg Zn, 12.05 kg Ca, 7.05 kg Al, 7.30 kg Fe, 2.50 kg K and 2.45 Na. 1 ton, 1:1 extract mixture, 121.64 kg of sulfur component went into solution.

Thus, the solution obtained from the demineralization reactions of CB_p is an important input in the manufacture of fertilizer as a plant nutrient raw material, as it contains potassium as well as rich zinc, sulfur and remarkable iron and calcium components. Zinc compound is an expensive substance with wide industrial use. Although the use of zinc element in plants as a fertilizer has proven to be extremely important for the plant and is used throughout the world, it cannot be used widely due to its high cost [27]. The use of zinc obtained from the recycling of scrap tyres in fertilizers will reduce the cost of fertilizer and increase the prevalence of zinc fertilizer.

Although the demineralization of pyrolytic carbon black will result in additional costs to the investor, it will be a sustainable and highly profitable project in terms of scrap tyre management, as demineralized carbon black with higher commercial value and also zinc that can be used for fertilizer will be obtained in the market. Thus, the bottleneck in the existing pyrolysis facilities will be overcome.

CONCLUSION

In this study, carbon black, one of the two main products obtained from the recycling of scrap tires by the pyrolysis method, was upgraded with an improved acid-base extraction method. Pyrolytic carbon black is very difficult to use industrially and find a market due to the high ash and carbon residues it contains. Since tire manufacturers use different carbon blacks and fillers such as SiO_2 in different tires and components, it is not possible to obtain carbon black that exactly matches the ASTM carbon black classification standard from pyrolytic carbon black upgrade studies. However, since carbon black that has better dispersion and dyeing intensity in the polymer and has the average qualities of carbon black within a certain range in the ASTM classification can be obtained, carbon black suitable for use in the polymer industry can be obtained.

It has been understood that when the tire sidewall and tread are pyrolyzed separately, two different types of carbon black can be obtained depending on the pore diameter, surface area and activity. In the upgrade study of CB_p, the ash amount of CB_p was reduced with a much higher efficiency than known acid-base methods.

Inorganic components obtained from carbon black are macro- and micro-nutrient elements that are vital for plants. The by-product (extraction and washing solutions) obtained from the CB_p upgrade study can be evaluated in the fertilizer industry and will reduce CB_p upgrade costs and provide a new perspective to the sector. Thus, pyrolysis facilities will come to the fore as a more feasible recycling method.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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