

Evaluation of solid product obtained from tire-derived fuel (TDF) pyrolysis as carbon black

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Received: 19 July 2013 / Accepted: 9 January 2014 / Published online: 31 January 2014
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Abstract The main focus of this study was quality improvement of solid product obtained from tire-derived fuel (TDF) pyrolysis to use it as a substitute for commercial carbon blacks. First of all, TDF samples were analyzed by means of proximate and ultimate analysis, heating value, X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. They were then pyrolyzed at a 400 °C pyrolysis temperature with 5 °C/min heating rate. After that, a two-stage improvement was performed on solid product to reduce its sulfur and ash content to that of commercial carbon black. As a result of this improvement process, the sulfur and ash content of the solid product was reduced to 0.22 and 0.27 % from 1.71 and 12.14 %, respectively. In addition, the XRD, SEM, atomic force microscopy, Brunauer–Emmett–Teller surface area, oil adsorption number and ICP-MS/MS analyses were performed for all products. The results were compared with different commercial carbon blacks. It was determined that the properties of the improved products were similar to those of commercial carbon blacks. These results suggest

that improved pyrolytic product of TDF can be used as a raw material by industries such as tire, plastic and paint manufacturing.

Keywords Carbon black · Pyrolysis · TDF

Introduction

The pyrolysis of tires has been investigated by several research groups who have demonstrated that the char has potential as a carbon black or activated carbon. The solid product can also be used as reinforcing filler for rubber goods and possibly as a printing ink pigment after appropriate treatment [1]. Li et al. [2] studied carbon dioxide activation for the solid product to have a high surface area such as activated carbon. Rodriguez et al. [3] compared solid product with carbon black. They realized that tire-pyrolysis residues could partially replace semi reinforcing commercial blacks for the preparation of rubber parts, such as footwear, conveyor belts, dock fenders, etc., which are not so high quality demanding as automotive tires. Waste tires were pyrolyzed to obtain carbon black under optimum conditions by Barbooti et al. [4] and Zabaniotou et al. [5]. The potential of polyisoprene rubber pyrolysis was investigated by Roy et al. [6]. Also, adsorption capacity of activated carbon obtained from pyrolysis of TDF was studied by Banar et al. [7] and Gupta et al. [8, 9]. In this context, the literature was reviewed related to especially improvement of carbon black and demineralization and desulfurization process of coal which are summarized in Table 1 [10–20].

Tire pyrolysis is alternative technology for carbon black production, but the economics of the process strongly depends on the commercial value of the pyrolytic carbon

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Table 1 Literature survey in related to improvement of carbon black and demineralization and desulfurization process of coal

Researchers	Experimental conditions			Explanations
	Material	Target content	Application	
Pantea et al. [10]	Pyrolytic carbon black	Carbonaceous deposits	Heating from 670 to 860 °C	The recovered pyrolytic carbon black (CBp) was heated in a post-pyrolysis process at temperatures ranging from 670 to 860 °C. In this study, the CBp was studied in comparison to a commercial tire carbon black and the CBp properties were correlated to their electrical conductivities. So, the electrical conductivity of CBp is lower than that of the commercial blacks
Zhou et al. [11]	Pyrolytic carbon black	Inorganic matters and carbonaceous deposit	Treating with HNO ₃ solution	It was studied that inorganic matters and carbonaceous deposit were removed by treating the pyrolytic carbon black with HNO ₃ solution. After that, the surface energy of washed pyrolytic carbon black modified by titanate-coupling agent (TWPC) was determined by inverse gas chromatography and it was found that TWPC has the great potential of applications in printing ink industry as pigment
Chaala et al. [12]	Pyrolytic carbon black	Ash	Treating with H ₂ SO ₄ and NaOH	Researchers were investigated the reduction of the ash content by sulfuric acid (H ₂ SO ₄) and sodium hydroxide (NaOH) treatment. And they compared the properties of the commercial carbon black filler grade N539 and those of the CBp recovered before and after the demineralization treatment
Bolat et al. [13]	Coal	Ash	Treating with HF, HCl, HNO ₃ , H ₂ SO ₄ and 0.5 N NaOH	Researchers were studied using different acids (HF, HCl, HNO ₃ and H ₂ SO ₄) alone and 0.5 N aqueous NaOH in combination with either one or two of the acids. It was found that the use of extraction with 0.5 N NaOH followed by leaching with 10 % HCl was the optimum approach for the chemical cleaning of the coal
Wu and Steel [14]	Coal	Ash	Treating with HF	Researchers were used hydrofluoric acid (HF) at 65 °C for coal demineralization and reduced the ash content from 5.30 wt% to 1.37 wt% by mainly removing Al and Si containing minerals. After that, subsequent leaching by ferric ions decreased the ash content further to 990 ppm by removing most of the pyrite and fluorides formed during the HF leaching
Karaca et.al. [15]	Coal	Sulfur	Treating with HNO ₃	The removal of pyritic sulfur from Turkish lignite in aqueous suspension by HNO ₃ was investigated and pyritic sulfur was quantitatively removed in 25 % HNO ₃ solution. It was observed that removal of pyritic sulfur increased with the increasing temperature and HNO ₃ concentration and decreasing particle size. Also, it was determined that the stirring speed has no effect at lower temperatures on the pyritic sulfur removal
Alam et.al. [16]	Coal	Sulfur	Treating with HNO ₃ and HCl	HCl and HNO ₃ were used, separately, to leach the floated coal, and the effectiveness of each acid on Mezino coal desulfurization was investigated. The total sulfur removal after flotation and leaching at optimum condition reached to 75.4 %. It was concluded that HNO ₃ was found to be much more effective than HCl
Mukherjee and Borthakur [17–19]	Coal	Sulfur	Treating with acid and alkali solutions	Researchers were investigated the effect of HCl, HNO ₃ and H ₂ SO ₄ at different concentrations on demineralization of high sulfur coal and it was found that HNO ₃ leads to maximum and H ₂ SO ₄ minimum desulfurization of the coal samples and the demineralization with the acids is relatively low. It was represented that alkali treatment was led to over 70 % removal of the inorganic sulfur in the coal samples

Table 1 continued

Researchers	Experimental conditions			Explanations
	Material	Target content	Application	
Vaccaro [20]	Coal	Ash and sulfur	Treating with HF, acetic acid, hydrogen peroxide, KOH, NaOH	It was expressed that generally, HF aqueous solution treatment reduced mineral matter of samples, but it had no effects on sulfur content. In particular, the best seems to be the combined treatment with acetic acid and hydrogen peroxide followed by the treatment with the weak base. The treatment with strong bases KOH and NaOH was appeared to be as much satisfactory

black. To increase to quality of pyrolytic carbon black, some improvement studies should be realized.

Therefore, in this study, waste tire pyrolysis was evaluated from an environmental perspective with a focus on the commercial utilization of the solid product. TDF samples 1–4 mm in size were pyrolyzed at a 400 °C pyrolysis temperature with 5 °C/min heating rate. Improvements of the solid product (SP) were performed to obtain a final product that had comparable physical and chemical properties with commercial carbon blacks. High abrasion furnace black (HAF) and fast extrusion furnace black (FEF) are the most widely used commercial carbon blacks in industry. HAF is structurally hard and is used for the production of cable, conveyor, outer tire, etc. FEF is soft and is used for the production of laying cables, tube tire, etc. [21, 22]. Unlike other studies in the literature, waste tires were formed into TDF before the pyrolysis processes to ensure homogeneity. Furthermore, a new improvement process was developed to obtain carbon black from the pyrolytic solid product.

Experimental methodology

In the experimental studies, raw material (TDF) was characterized. Then, TDF was pyrolyzed and improvement studies were performed on the solid product. Finally, the products were characterized and compared with commercial products. Analysis methods are described in their own sections.

Characterization of raw material (TDF)

The TDF used for pyrolysis was prepared from the shredded mixture of *cis*-butadiene rubber (CBR) and styrene butadiene rubber (SBR) steel-free tire samples that were supplied from a tire recycling plant. This shredded mixture was crumbed and sieved to produce a size range of 1–4 mm. The moisture, ash, volatiles and fixed carbon content of the TDF sample were determined by ASTM D-3173-85, ASTM D-3174-12, ASTM D-3172-73 and

Table 2 Composition of TDF and different waste tires

Analysis	TDF	Waste tire		
		Cunliffe and Williams [23]	Rodriguez et.al. [3]	Murillo et.al. [24]
Elemental analysis (wt%)				
Carbon	82.52	86.4	88.64	83.92
Hydrogen	6.94	8.0	8.26	6.83
Nitrogen	0.47	0.5	0.43	0.78
Sulfur	1.70	1.7	1.43	0.92
Proximate analysis (wt%)				
Moisture	0.84 ± 0.02	1.3	0.94	0.75
Ash	9.63 ± 0.21	7.1	3.83	4.16
Volatiles	65.45 ± 0.25	62.2	64.09	64.97
Fixed carbon	24.08 ^a	29.4	31.14	30.08
HHV (MJ kg ⁻¹)	37.46 ± 0.2	40	–	38.6

^a By difference

ASTM D-3175-82, respectively. The elemental composition and higher heating value (HHV) of the TDF were determined using a CHNS-O Elementar Vario EL III and IKA C200 calorimeter (ASTM D-5865), respectively.

The comparative results of elemental analysis, proximate analysis and HHV of the TDF and different waste tires are listed in Table 2. The results of the TDF sample were similar to the values in the literature except for the ash value.

To identify the morphologic structure (crystalline/amorphous) of TDF, diffraction experiments were performed with a Rigaku Rint 2200 diffractometer (40 kV, 30 mA) using CuK α radiation (Fig. 1a). Diffractograms illustrated S (jcdp no. 00-020-1227), SiO₂ (jcdp no. 00-043-0596) and ZnO (jcdp no. 00-036-1451) signals in the TDF. SiO₂ in the TDF samples results from tire manufacturing while ZnO and S result from the vulcanization of the tire.

A ZEISS SUPRA 50 VP scanning electron microscope (SEM) was also used to obtain SEM micrographs of the

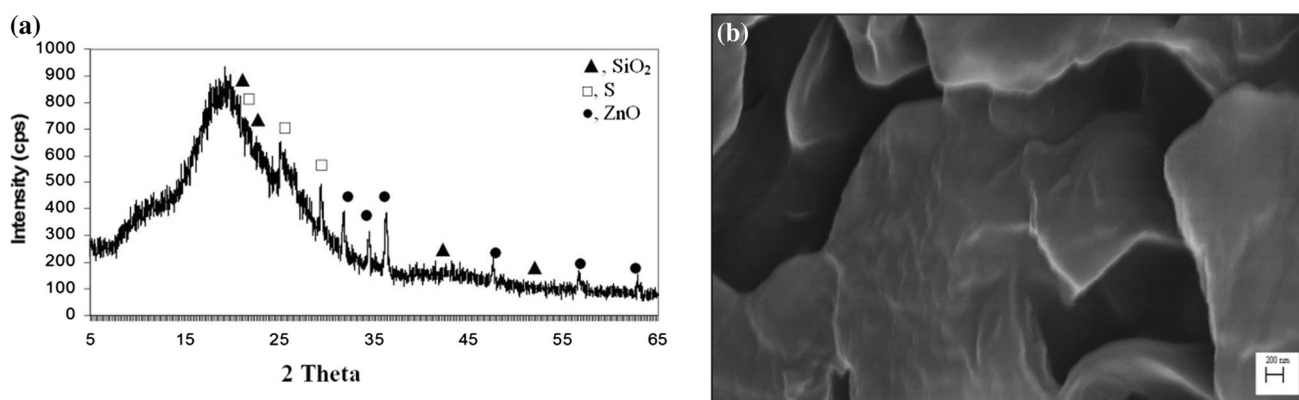


Fig. 1 a XRD spectra of TDF. b The SEM images of TDF (50,000 \times)

TDF, which was prepared by gold coating to enhance electrical conduction. In Fig. 1b, the flat structure of the TDF can be observed.

TDF pyrolysis

Pyrolysis experiments were carried out under atmospheric pressure at a 400 °C pyrolysis temperature with 5 °C/min heating rate in a fixed-bed stainless steel (380 S) 240 cm³ reactor (well-swept with nitrogen). Pyrolysis conditions were determined based on the extensive experimental works conducted by Akyıldız [21]. The reactor was surrounded with a resistive oven (400 W). All experiments were performed in triplicate. In a typical run, a 10-g sample was placed into the reactor which was heated until it reached the set temperature, which was maintained for 1 h. Solid and liquid product yields were determined in each experiment by weighting. The gas yields were determined by the mass difference. All the yields were expressed on a dry basis and the average yields of at least three experiments were within an experimental error of less than ± 1 wt. %. Pyrolysis product yields for solid, liquid and gas were 34, 38.8 and 27.2, respectively at 400 °C with 5 °C/min heating rate.

Improvement of the solid product

After the solid product was obtained by pyrolysis, physical and chemical analyses were carried out to assess its quality as a carbon black (see “[Characterization of products](#)”). It was observed that the sulfur (1.71 %) and ash contents (12.14 %) of the solid product were higher than those of commercial carbon blacks. The ash values were similar to those reported by Zolezzi et al. [25]. However, these values were lower than those obtained by Helleur et al. [26] whereas higher than those reported by MuiEdward et al. [27] and Uçar et al. [28]. Therefore, the solid product obtained from tire pyrolysis needs to be demineralized. For

that reason, a leaching procedure for demineralization and desulfurization was performed on the solid product with HCl (Merck, 37 %), HNO₃ (Merck, 65 %) and HF (Sigma-Aldrich, 40 %) as shown in Fig. 2. First, HCl, HNO₃ and mixture of HCl and HNO₃ were experimented for these processes. In this trial, 0.5 grams of solid product (SP) was mixed with 10 ml of concentrated acid [(HCl, HNO₃ and HCl + HNO₃ (1:1, v:v)] solutions. Sample solutions were digested in a microwave oven (CEM MARS 5, 400 W). The temperature of each sample was raised to 175 °C in 6 min and remained there for 10 min before cooling down to room temperature over 15 min. At the end of the microwave program, the mixture was separated by filtration, and then washed with distilled water until the pH value of filtered water was neutral. Finally, the product was dried and weighed, and the ash and sulfur content were determined according to ASTM D-3174 and ASTM D-1619, respectively. Based on the results of this step, it was decided that a mixture of HCl and HNO₃ solutions would give the highest removal efficiency. The SP was then digested with different concentrations of HCl + HNO₃ mixture (90–10 % with 10 % intervals) in the microwave to determine the optimum mixture. Ash and sulfur analyses of the acid digested products were carried out and the optimum mixture was determined from the sulfur content. The product with sufficient sulfur was called the intermediate product (IP). Although, the IP reached commercial carbon black sulfur quality, ash was found to be rather difficult to remove and it was necessary to use HF extraction. Therefore, the IP was digested with different concentrations of HF solutions (100, 90, 80 and 70 %). For this procedure, 1 gram of IP was mixed with 10 ml of the HF solution to be tested, and the mixture was digested on a hotplate until a solid form was obtained. The solid forms were washed with distilled water until the pH value of the filtrate was neutral. Next, the washed fractions were dried, weighed and their ash contents were determined. In this manner, the optimum HF concentration that gave sufficient

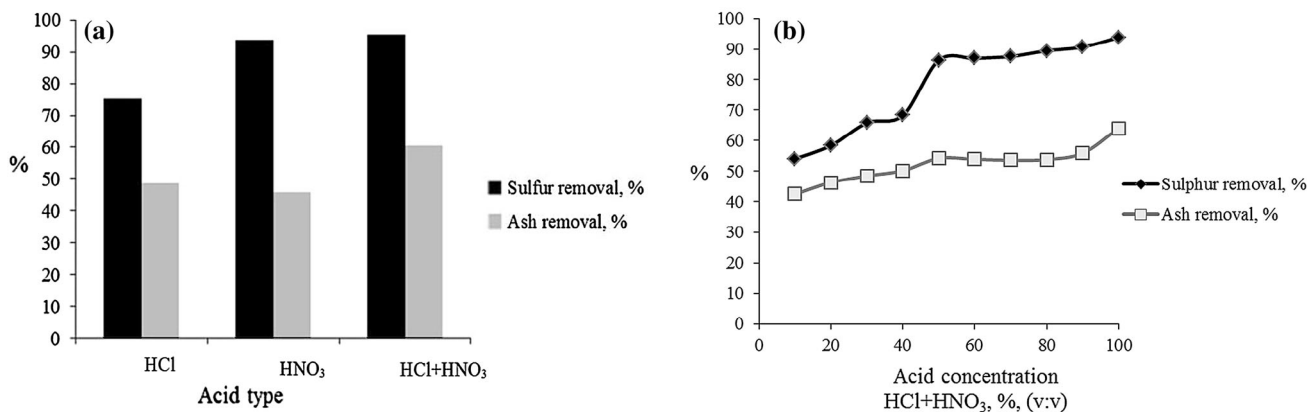


Fig. 2 a Demineralization and desulfurization yields of SP by acid treatment. b The effects of different acid ratios on ash and sulfur removal

ash content was determined. The resulting product with a sufficient ash content formed by HF processing was called the final product (FP). Afterwards, the physical and chemical properties of the obtained solid, intermediate and final products were determined and compared with different commercial carbon blacks (HAF N330 and FEF N550) that are produced by the furnace technique.

Characterization of products

To identify the physical structure of the products, the moisture, ash, volatiles and fixed carbon content, elemental composition and HHV of each product were determined using the same procedures for TDF characterization mentioned above. In addition to these analyses, the pH and density values were also determined according to ASTM D 1512 and ASTM D 1513, respectively.

XRD and SEM analyses were carried out similarly to TDF analysis. Surface morphology images for the SP, IP and FP were obtained using a Q-scope 250 atomic force microscopy (AFM) from Quesant instruments with standard silicon cantilevers (Quesant). Topography images were collected in noncontact mode at a scan rate of 4 Hz under ambient laboratory conditions.

The nitrogen adsorption measurements (BET, Brunauer–Emmett–Teller) for the SP, IP and FP were performed with a Quantochrome Autosorb 1-C. Before the adsorption measurements, the samples were outgassed for 17 h at 300 °C in vacuum.

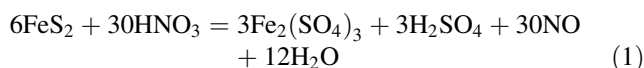
The oil adsorption number (OAN) gives information about how hard or soft carbon black is. This metric is important for many applications of the carbon black. OAN analysis for the SP, IP and FP was performed according to ASTM D2414, and the results were compared with commercial carbon black values. The OAN value of the SP is not available in this analysis because of its large particle size.

The quantitative analysis of all products and commercial carbon blacks was conducted using an ICP-MS/MS (Agilent 8800) after extracting with a microwave according to Stals et al. [29].

Results and discussion

Results of the improvement studies

Results of the SP demineralization and desulfurization with 100 % HCl, HNO₃ and HCl + HNO₃ (1:1, v:v) are shown in Fig. 2a as a function of acid type. As shown as Fig. 2a, HNO₃ and HCl + HNO₃ treatments were very effective at sulfur removal (93.6 and 95.3 %, respectively). Although treatment with only HCl did not yield high removal efficiency (75.4 %), it provided sufficient reduction in sulfur content when compared with commercial carbon blacks (0.5 %). The content of sulfur in carbon black could reach more than 80 % of total sulfur in tire. Inorganic sulfides such as FeS₂ and ZnS as well as elemental sulfur have been identified in the carbon black [28]. Kumar and Hari Shankar [30] indicated that pyrite (FeS₂) can react with dilute nitric acid solution at moderate temperature and strong oxidizing conditions (such as high concentration) although it is almost unaffected by hot and concentrated HCl. Equation (1) explains the reaction between FeS₂ and high concentrated HNO₃ [30]. In addition to this, the results of this study show that also concentrated HNO₃ is more effective than the concentrated HCl to oxidize sulfur.



For ash removal, extraction with HCl and HNO₃ gave efficiencies of 48.8 and 45.9 %, respectively. The demineralization in HCl acid treatment is expected due to removal of soluble components of mineral matters. The

Table 3 The effects of HF on the ash removal

	Initial value	HF (%)			
		70	80	90	100
Ash content (%)	5.56	0.51	0.53	0.36	0.27
Ash removal (%)	–	90.8	90.5	93.5	95.1

removal of mineral matter by HCl acid brings an increase in surface area due to creation of new pores of small and intermediate size. On the other hand, as indicated by Kumar and Hari Shankar [30] an appreciable reduction in surface area of micropores and mesopores at higher concentration of HNO₃ acid solution is expected, giving resistance to the penetration of HNO₃ acid into the matrix, and thus contributes in impeding the extent of demineralization. Although reported individual reverse effects of HCl and HNO₃ [30], in this study, the mixture of HCl and HNO₃ gave the highest demineralization efficiency (60.5 %). It is thought that due to the new pores generation by HCl, HNO₃ could penetrate into the matrix. In addition to this, HCl has better affinity for Zn more than that of HNO₃. Consequently, it was decided that HCl and HNO₃ mixture was the best solution for the demineralization and desulfurization process.

To determine the optimum concentration, the SP was digested in the microwave using different concentrations of the HCl + HNO₃ mixture. The ash and sulfur contents of the acid digested products are given in Fig. 2b. As shown in Fig. 2b, 50 % HCl + HNO₃ concentration was the optimum concentration because it resulted in sufficiently low sulfur content (0.22 %). Although this product, IP, had a good quality in terms of sulfur, it still had higher ash content (5.56 %) than commercially available carbon black (0.2 %).

The IP was digested with different concentrations of HF solutions. Table 3 shows the final ash content of the products according to various HF concentrations. As shown in this table, 100 % HF concentration reduced the ash content from 5.56 to 0.27 %, resulting in a removal efficiency of 95.1 %. The resulting product was designated the final product (FP). Although, HF aqueous solution treatment reduced mineral matter of samples, silicate based minerals, it had no effects on sulfur content as indicated in Vaccaro's study [20]. Therefore, sulfur content of the IP product did not change after HF treatment.

Characterization of the products

The properties of all products (SP, IP and FP) and commercial carbon blacks (HAF and FEF) are given in Table 4. The weight yield of the products according to TDF sample on dry ash free basis was determined as 34.00 % for SP,

Table 4 Properties of the products

	SP	IP	FP	HAF	FEF
Weight yield (%) ^a	34.00	31.76	29.97		
Moisture (wt%)	1.25	1.36	1.35	1.74	0.2
Ash (wt%)	12.14	5.56	0.27	0.79 (0.2 ^b)	0.64 (0.2 ^b)
Volatiles (wt%)	15.69	17.06	19.56	10.19	12.01
Fixed carbon (wt%)	70.92	76.02	78.82	87.28	87.15
Sulfur (%)	1.71	0.22	0.22	0.53 (0.5 ^b)	0.49 (0.5 ^b)
Density (g/L)	271.03	384.6	404.6	405.67	397.74
pH	9.22	5.5	5.3	6.72	7.8
HHV (MJ kg ⁻¹) (daf)	42.95	43.83	46.55	33.47	33.91

SP solid product, IP intermediate product, FP final product, HAF high abrasion furnace black, FEF fast extrusion furnace black

^a According to TDF sample on dry ash free basis

^b Commercial results taken from producer web site (<http://www.tupras.com.tr/detailpage.tr.php?IPageID=572> and <http://www.tupras.com.tr/detailpage.tr.php?IPageID=578>, in Turkish)

31.76 % for IP and 29.97 % for FP after pyrolysis, HCl + HNO₃ and HF treatments, respectively. As it can be seen from Table 4, ash and sulfur contents of the products are decreased after treatments while fixed carbon contents are increased. Volatiles are given in Table 4 as received basis. When the volatile matter content of the products was calculated on the dry ash free basis (daf), the results were found to be 18.18 %, 18.33 and 19.88 % for SP, IP and FP, respectively. As it can be seen from data HCl + HNO₃ and HF treatments did not affect the volatile matter content, significantly. Ash removal in the improvement studies caused an increase in fixed carbon content and therefore HHV value of the IP and FP increased. The pH decreased with the acid extraction, and density increased with decreasing particle sizes. In addition, XRD, SEM, AFM, BET and OAN (ASTM D2414) analyses of the SP, IP, FP and commercial carbon blacks (HAF and FEF) were performed.

XRD spectra of the solid product that show Si and ZnS content are given in Fig. 3a. It has been reported that the ZnO and sulfur present in tire react during pyrolysis to form ZnS [28] and reaction between sulfur and zinc combined with other minerals in tire rubber such as Ca, Fe and Si eventually increases the ash content in the final product [31, 32].

The XRD results of the improved products (IP and FP) and commercially available carbon blacks (HAF N330 and FEF N550) are given in Fig. 3b and c, respectively. As a result of the improvement process, the XRD patterns of the IP and FP are similar to commercially available carbon

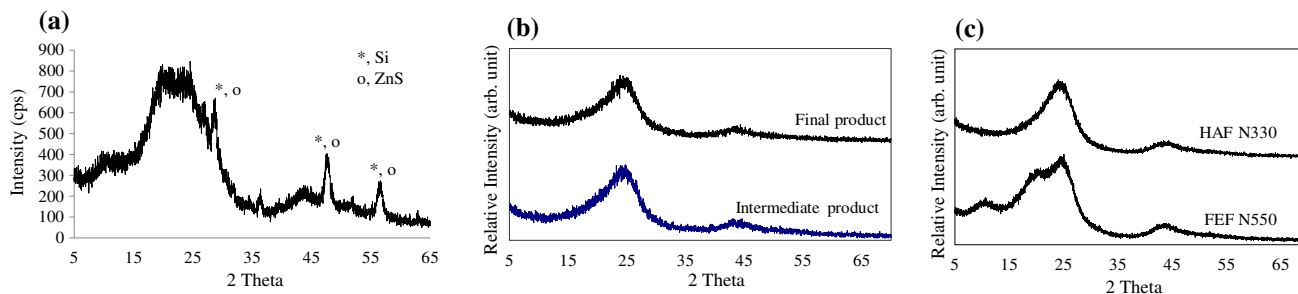


Fig. 3 XRD spectra of the **a** solid product, **b** improved products, **c** commercial carbon blacks

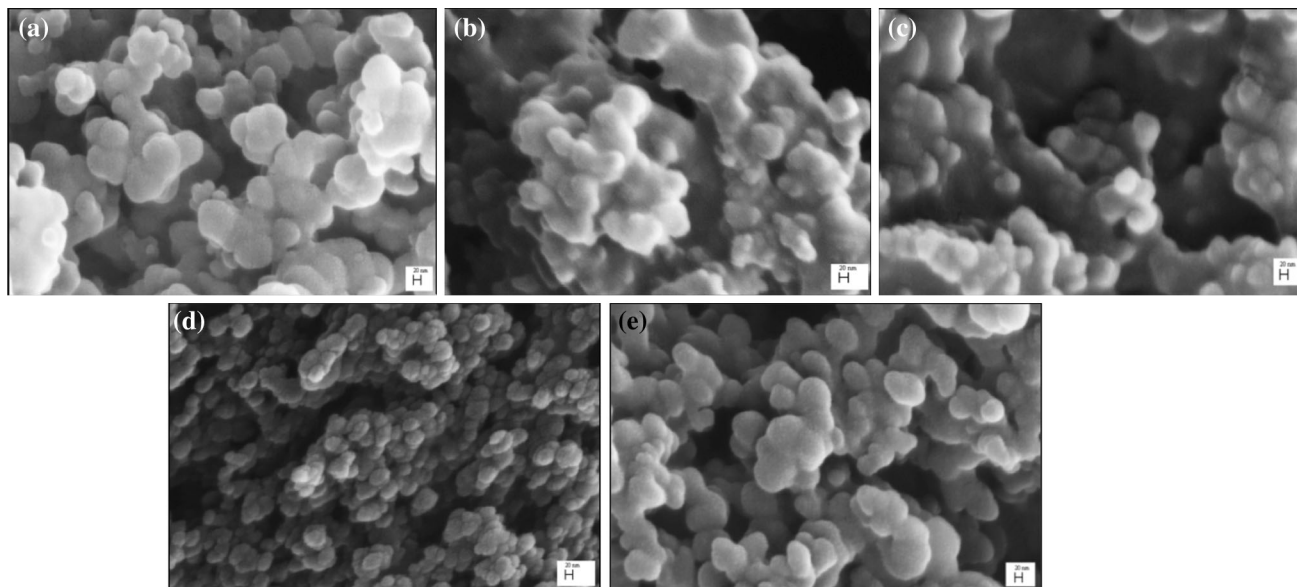


Fig. 4 The SEM images (300,000 \times) for the **a** SP, **b** IP, **c** FP, **d** HAF N330 and **e** FEF N550 samples

black because the removal of the Si and ZnS peaks. According to the XRD patterns of carbon blacks, it was observed that the commercial carbon blacks had an amorphous structure containing only carbon atoms (jcdp no. 00-026-1081).

The SEM images of the SP, IP, FP, HAF N330 and FEF N550 are given in Fig. 4, respectively. As shown in these figures, the SP has a sintered and porous structure resulting from pyrolysis while TDF has a flat structure (Fig. 4a). The SP particle size was between 40 and 100 nm. Figure 4 b and c shows that the particle size of the IP and FP were 60 and 50 nm, respectively, and their particle sizes are similar to the particle size of HAF N330 and FEF N550 (50 and 75 nm, respectively) (Fig. 4d, e). The smaller particle sizes of the IP and FP than the SP indicate that the improvement process also decreased the particle size. It was also observed that all product stages and commercial carbon blacks are similar to each other in terms of structure.

The AFM images for the SP, IP, FP, HAF N330 and FEF N550 are given in Fig. 5, respectively, in micrometer

scale. As seen in Fig. 5a, the SP does not show a regular particle size distribution because of agglomeration. This heterogenic structure resulted from the tendency of nano-sized particles to agglomerate in the SP. The average height is between 100 and 200 nm and the roughness is 135.2 nm. The top points of the IP, FP, HAF N330 and FEF N550 were 517, 199.7, 383.5 and 513.4 nm as shown in Fig. 5b–e respectively. The particles of HAF N330, FEF N550 and the various stage products agglomerated quickly. According to these results, the particle size was decreased with HF application.

The BET and OAN results of products are given in Table 5. The BET surface area of the SP is 105 m²/g. Li et al. [2] and Zhang et al. [33] found that the BET surface area of the solid product of waste tire pyrolysis was 89 and 68 m²/g, respectively. The BET value in this study is higher than that observed in previous studies in the literature. When compared with HAF N330 (178 m²/g) and FEF N 550 (46 m²/g), the surface area of the SP was intermediate between these values. An increase was observed in

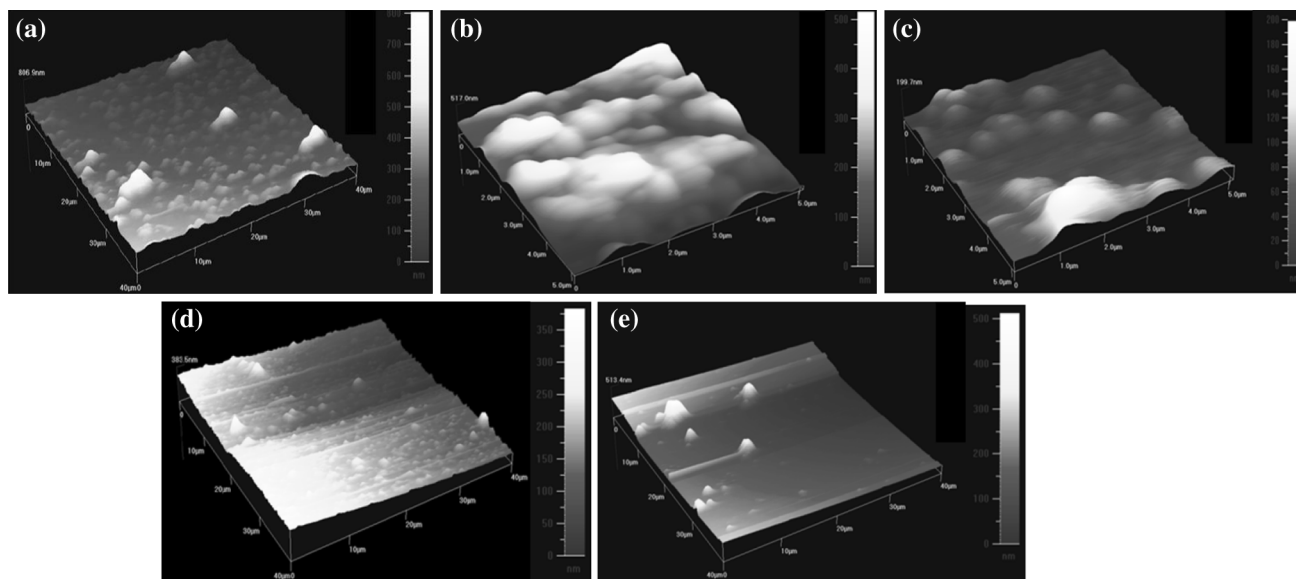


Fig. 5 AFM images ($5 \times 5 \mu\text{m}$) for the **a** SP, **b** IP, **c** FP and ($40 \times 40 \mu\text{m}$) for the **d** HAF N330, **e** FEF N550 samples

Table 5 The BET and OAN analysis results

	SP	IP	FP	HAF N330	FEF N550
BET (m^2/g)	105	185	212	178	46
OAN ($\text{ml}/100 \text{ g}$)	Not available	103	101	88 ^a	83 ^a

SP solid product, IP intermediate product, FP final product, HAF high abrasion furnace black, FEF fast extrusion furnace black

^a These values were given from producers

BET values from the SP to the FP. This resulted from acid extraction, which decreased the particle size, resulting in an increase in the surface area. In addition, the BET value of the IP and FP (185 and 212 m^2/g , respectively) were higher than commercial carbon black. It was not possible to carry out OAN analysis on the SP because of its large particle sizes. On the other hand, as shown in Table 5, the OAN values of the IP and FP are similar to each other and higher than those of the commercial carbon blacks. This result indicates that the IP and FP structures are softer than the HAF and FEF samples since an increasing OAN indicates a softening of the material and a decrease in particle size. BET and OAN are important parameters for the useable area of carbon black in many applications.

The quantitative analysis results for Al, Fe, Mn, Sr and Zn obtained from ICP-MS/MS are given in Table 6. These elements (with exception Zn) are considered contaminants for carbon black and they need to be controlled in industry in view of risks to change carbon black properties [34]. According to table, the concentrations of the elements in

Table 6 ICP-MS/MS results of the products and commercial carbon blacks

	TDF	IP	FP	HAF	FEF
Al ($\mu\text{g}/\text{g}$)	609	93.6	35.2	32.5	44.7
Fe ($\mu\text{g}/\text{g}$)	687	657	107	39	71
Mn ($\mu\text{g}/\text{g}$)	18.9	5.1	1.9	0.5	2.6
Sr ($\mu\text{g}/\text{g}$)	94.3	8.8	3.5	3.2	13.4
Zn ($\mu\text{g}/\text{g}$)	38,692	1,490	384	46.5	599

the products are decreased with improvement studies. Also, Zn concentration of the final products can be tolerated according to commercial carbon blacks while the values of the final products are lower than those of the commercial carbon blacks.

Conclusion

In Turkey, annually about 8 million tires are produced and an estimated 284,800 tons/year of tire waste must be disposed. The total capacity of the facilities for recovering waste tires as granulated material is 101,000 tons/year. Moreover, the total capacity of the cement plants licensed for using waste tires as alternative fuel for energy recovery is 130,000 tons/year [35]. Among these recovery applications, recently there is no plant that produce carbon black from waste tires in Turkey although the pyrolysis method is classified in the section of applicable recovery methods for waste tires titled “regulation for control of the tires which have completed their life-cycles (TCL)” that was published

in the Official Gazette on 25 November 2006, number 26357 in Turkey. From this point of view, it was mainly focused on the quality improvement of solid product obtained from TDF pyrolysis to use it as a substitute for commercial carbon blacks. Experiments of the study have shown that:

- Solid product of the pyrolysis should be improved in term of the sulfur and ash contents to reach the quality of commercial carbon black. To achieve this quality level, it was seen that the solid product should be treated with 50 % concentration of HCl and HNO₃ mixture followed by the treatment with 100 % concentration of HF. After this processing, the final product had sufficiently low ash and sulfur contents (0.27 and 0.22 %, respectively), which were similar to commercial carbon black.
- XRD patterns determined that ZnO and S which are built in TDF were converted to ZnS and Si during the pyrolysis. These patterns also showed that acid treatment of the solid product also provided ZnS and Si removal.
- According to the SEM images, the solid product may be useful for applications which require a high surface area and porous structure (e.g., as an activated carbon) since its particle size is between 40 and 100 nm. Furthermore, SEM images show that acid treatment of the solid product decreased the particle size and provided similar particle size and structure to solid product with commercial carbon blacks have.
- BET analysis showed that acid treatment increased the BET surface area of the solid product. It was also observed that surface area of the acid-treated solid product was higher than that of the commercial carbon blacks.
- OAN values of the acid-treated solid products were found to be higher than those of the commercial carbon blacks. This result indicates that the acid-treated solid products have a softer structure and smaller particle size than commercial carbon blacks.

As a conclusion, in this study, a final product which has sufficiently similar properties to commercial carbon black was obtained through pyrolysis of TDF followed by a novel improvement process. This new and valuable product can be used as a raw material by many industries, including those involved in tire, plastic and paint manufacturing.

Acknowledgments This study was supported by TUBITAK (The Scientific and Technological Research Council of Turkey) under the Grant No.: 108Y267 and Anadolu University Scientific Research Projects Commission under the Grant No.: 080237. In addition, the authors thank Prof. Dr. Nuran Ay, Prof. Dr. Ö. Mete Koçkar and Prof. Dr. Servet Turan for their valuable contributions.

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