# Thermal plasma pyrolysis of used tires for carbon black recovery

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This letter reports on the gaseous and carbon black product characteristics from nitrogen thermal plasma pyrolysis of used tires. Recently the disposal of used tires has drawn considerable attention because of the large amount of used tires produced all over the world. Several options for dealing with waste tires exist, such as using as shielding in shipside, incineration and pyrolysis. Thermal plasma pyrolysis of used tire has several advantages over other alternative tire recycling methods. No toxic substances are emitted, no liquid product is generated in the process and various commercial applications for the gaseous and solid products obtained are possible. A number of studies [1–4] have shown the merits of the plasma pyrolysis technique dealing with some classes of waste material especially polymers. In plasma pyrolysis, the organic volatile matter of tires is decomposed to low-molecular-weight products, which are useful as fuels or chemical sources; the inorganic components and the carbon black filler are discharged as solid residue relatively unaltered and therefore can theoretically be recycled in carbon black related applications.

In the current study, the used tire particle sample was provided by Guangzhou Resource Recycling Company. A fine fraction of particles between 30 and 80 mesh was used in the experiments. Detailed description of the reactor assembly has already been published [1]. Steam may be injected into the plasma reaction chamber with the feed particles. The gas products were collected in rubber bags and analyzed by gas chromatography (Shimadzu GC-20B-1). Solid residues were saved in the ash tank. Samples $CB_{p1}$ and $CB_{p2}$ were obtained from plasma pyrolysis of tires at 35.2 kVA, feed rate 80 g/min, without steam injection and with steam injection $80 \times 10^{-6}$ $m^3$/min, respectively. Since the solid residues were studied for substitution of commercial carbon black, the following analyses were carried out: BET surface area, ash-content, SEM, XPS and $^{13}$C-NMR.

When tire particles are injected into the plasma, they are heated up very rapidly by the plasma, the volatile matter is released and cracked giving rise to $H_2$, CO, $C_2H_2$ and other light hydrocarbons. Typical data are given in Table I, from which we can see that $H_2$ and CO are the main products. By steam injection, the content of $H_2$ is increased from 14.2 to 24.1% and CO is increased from 3.2 to 14.2%. The gas product from plasma pyrolysis with steam may be utilized in syngas applications.

TABLE I Product distribution from plasma pyrolysis of tires (Power input: 35.2 kVA; Feed rate: 80 g/min; steam injection: $80 \times 10^{-6}$ $m^3$/min)

| | Concentration (vol.%) | |
|---|---|---|
| Product | Without steam injection | With steam injection |
| $H_2$ | 14.2 | 24.1 |
| CO | 3.2 | 14.1 |
| $C_2H_2$ | 3.9 | 1.8 |
| $CH_4$ | 1.0 | 1.0 |
| $C_2H_4$ | 0.5 | 0.4 |
| $N_2$ | 71.6 | 52.4 |
| $C_nH_m$ + unknown | 5.6 | 6.2 |
| Solid residue yield | 57.8 (wt%) | 23.0 (wt%) |
| Gas yield | 42.2 (wt%) | 77.0 (wt%) |

Table I also shows the products distribution. Tires contain approximately 25–30% of carbon black filler and 5% of inorganic components on a steel-free basis. The inorganic tire components usually end up in the solid residues, thus, if no carbonaceous deposits are formed, tire pyrolysis should yield approximately 30–35% pyrolytic carbon black ($CB_p$). High $CB_p$ yields indicated the formation of carbonaceous deposits during the pyrolysis. It should be noted that without steam injection, the yield of the $CB_{p1}$ is much higher than the theoretical values expected from concentration of the virgin carbon black in the tires. With steam injection, the yield of the gas reaches up to about 77%, while the yield of the $CB_p$ is about 23%, which is lower than the concentration value of the virgin carbon black in the tires. These changes indicated that there are some chemical processes occurring during

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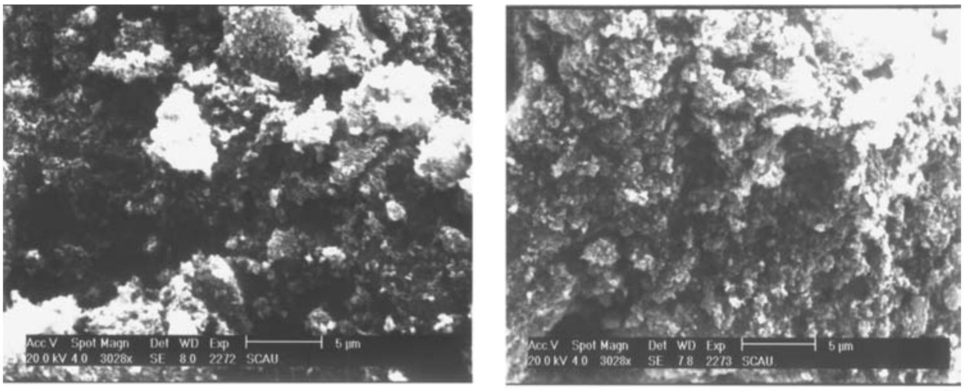


(a) (b)

*Figure 1* SEM photos of (A) $CB_{p1}$ from tires plasma pyrolysis at 35.2 kVA, feed rate 80 g/min and (B) $CB_{p2}$ from tires plasma pyrolysis at 35.2 kVA, feed rate 80 g/min, steam injection: 80 ml/min.

plasma gasification when injecting steam, and the reaction between carbon and steam may play a significant role in the pyrolysis process, such as $C + H_2O \rightarrow H_2 + CO$.

However, such mass balance only allows a rough estimate of the $CB_p$ quality. Since it is critical to find commercial applications for the $CB_p$ derived from a tire pyrolysis process, the properties of $CB_{p1}$ and $CB_{p2}$ samples were compared with those of commercial carbon black in Table II. The $CB_p$ has surface areas comparable to those of commercial carbon black such as series N330, but it has a great proportion of ash impurities. In commercial carbon blacks, the ash-content must be below 0.5 wt% to be admissible for tire manufacture. According to Piskorz *et al.* [5], one-half of the inorganics could be removed by acid wash if desired. Elemental analysis result shows that the H/C atomic ratio of the tires particle is 1.09, while the H/C atomic ratio of the pyrolytic $CB_{p1}$ is 0.061; by injecting equivalent steam, the pyrolytic $CB_{p2}$ obtained exhibited a H/C atomic ratio of 0.034. The result is lower than that obtained by conventional pyrolysis [6] and it is closer to the value 0.025 of the H/C atomic ratio of the commercial tire carbon black.

SEM photos of $CB_{p1}$ and $CB_{p2}$ are shown in Fig. 1. Compared with standard carbon black, the particle sizes are similar and in both cases the morphology of the carbon black changed only slightly in the thermal plasma pyrolysis process.

Using X-ray photoelectron spectroscopy (XPS) PHI-5300/ESCA, wide scan spectra in the binding energy range 0–1000 eV were obtained to identify the surface elements present. Typical XPS wide scan spectra of the samples are shown in Fig. 2; only minor differences were observed between the spectra of $CB_{p1}$ and $CB_{p2}$. The spectra are dominated by the $C_{1s}$ photoelectron peak, representing the major constituent of the carbon black; small signals confirm that oxygen and sulfur are

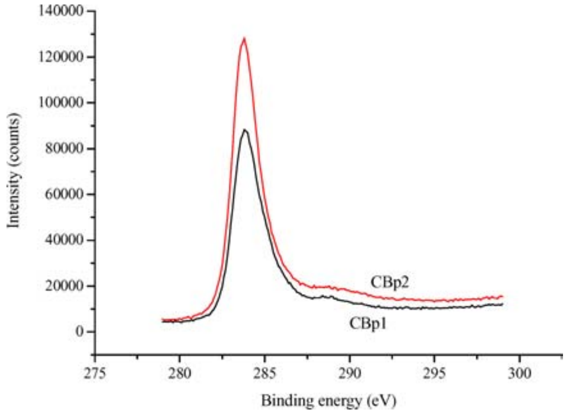


*Figure 2* XPS wide scan spectra ($CB_{p1}$ and $CB_{p2}$ sample).

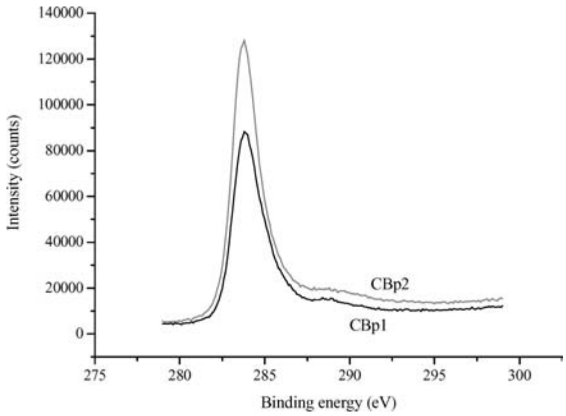


*Figure 3* XPS narrow scan of $C_{1s}$.

TABLE II Ultimate and proximate analysis of solid residue

| | Ultimate analysis (wt% dried) | | | | | Ash (wt% dried) | BET surface area | H/C atomic ratio |
|---|---|---|---|---|---|---|---|---|
| Materials | C | H | O | N | S | | $m^2/g$ | |
| Tire particle | 80.5 | 7.33 | 10.27 | 0.33 | 1.574 | 8.97 | – | 1.09 |
| $CB_{p1}$ | 82.69 | 0.42 | 13.9 | 0.42 | 2.57 | 15.14 | 64.8 | 0.061 |
| $CB_{p2}$ | 85.06 | 0.24 | 12.35 | 0.38 | 1.97 | 16.25 | 70 | 0.034 |
| Carbon black N330 | 97.1 | 0.2 | 1.1 | 0.2 | 1.0 | 0.4 | 80 | 0.025 |

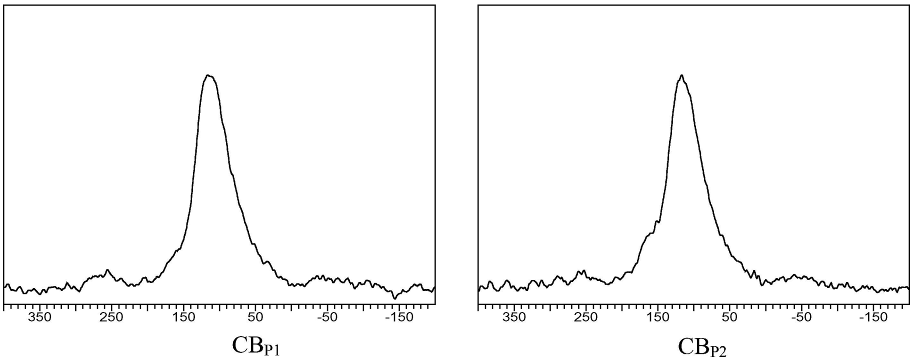


*Figure 4* Comparison of the $^{13}$C-MAS-NMR spectra of $CB_{p1}$ and $CB_{p2}$.

also present in the surface region as well as peaks of other elements such as Zn, Cu, Al. The $C_{1s}$ narrow scan spectra are presented in Fig. 3. According to Darmstadt *et al.* [7] the more complete the graphitic structure is, the smaller the full width at half-maximum (FWHM) of the $C_{1s}$ peak will be. The FWHM of the $C_{1s}$ peak of sample $CB_{p1}$ is 2.1 eV, and that of $CB_{p2}$ is 1.9 eV, indicating that pyrolytic carbon black obtained from plasma pyrolysis with steam injection has a more complete graphitic structure. Probably, aliphatic or adsorbed hydrocarbon compounds on the $CB_p$ surface can react with steam and thus are oxidized/removed, resulting in a higher graphitization degree of $CB_p$.

The bulk carbon chemistry was studied by $^{13}$C-MAS-NMR performed with a Bruker DSX 300 spectrometer at a carbon frequency of 75.47 MHz and a spinning frequency of 10 kHz. The 90° pulse width was 4 $\mu$ s and high power proton decoupling was performed during recording of spectra. The chemical shifts $\delta$, expressed in ppm were referenced relative to the signal of admantane at $\delta_c = 38.3$ ppm. The recycle delay was 20 s and 1800 scans were co-added for each spectrum. The spectra of $CB_{p1}$ and $CB_{p2}$ are presented in Fig. 4. A broad peak with a chemical shift of approximately 116 ppm can be seen, which is similar with the $^{13}$C-MAS-NMR spectra of commercial carbon black [8]. A broad shoulder at approximately 151 ppm is presented for $CB_{p2}$. Both of these two samples are dominated by the aromatic C=C bonds at about 116 ppm, the C=C peaks account for about 90% of total area. With steam injection, the C=O intensity increased. The concentration of aliphatic carbon atoms is very small in the $CB_p$ samples.

In conclusion, thermal plasma processing can be utilized to convert used tires to useful gases and pyrolysed carbon black. Our results have shown that the pyrolysis gas can be used as syngas; the $CB_p$ has a surface area and microstructure very similar to the commercial carbon black. A substitution of commercial carbon black by $CB_p$ for certain applications should be technically possible.

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