

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236655751>

Recycling Plastics as a Resource for Electric Arc Furnace (EAF) Steelmaking: Combustion and Structural Transformations of Metallurgical Coke and Plastic Blends

ARTICLE *in* ENERGY & FUELS · JANUARY 2010

Impact Factor: 2.79 · DOI: 10.1021/ef900875r

CITATIONS

9

READS

111

6 AUTHORS, INCLUDING:



[Veena Sahajwalla](#)

University of New South Wales

148 PUBLICATIONS 772 CITATIONS

[SEE PROFILE](#)



[Somoyote Kongkarat](#)

Thammasat University

11 PUBLICATIONS 48 CITATIONS

[SEE PROFILE](#)



[Rita Khanna](#)

University of New South Wales

106 PUBLICATIONS 442 CITATIONS

[SEE PROFILE](#)



[Narendra Saha-Chaudhury](#)

University of New South Wales

38 PUBLICATIONS 196 CITATIONS

[SEE PROFILE](#)

Recycling Plastics as a Resource for Electric Arc Furnace (EAF) Steelmaking: Combustion and Structural Transformations of Metallurgical Coke and Plastic Blends

Veena Sahajwalla,[†] Magdalena Zaharia,^{*,†} Somyote Kongkarat,[†] Rita Khanna,[†]
N. Saha-Chaudhury,[†] and Paul O’Kane[‡]

[†]School of Materials Science and Engineering, The University of New South Wales, Sydney, New South Wales 2052, Australia, and [‡]Onesteel, Rooty Hill, Sydney, New South Wales 2766, Australia

Received August 12, 2009. Revised Manuscript Received September 21, 2009

Recycling end of life products, such as waste tires and waste plastics in iron- and steelmaking permits their use as energy and material resources. The current paper discusses the combustion efficiencies of blends of metallurgical coke (MC) with plastics for electric arc furnace (EAF) steelmaking. Laboratory tests involved the combustion in a drop tube furnace (DTF) at 1473 K of MC premixed with different proportions of plastics, polypropylene (PP), and high-density polyethylene (HDPE) (10–30%) under a 20% O₂ and 80% N₂ gas mixture. In the tested conditions, coke–plastic blends indicated higher combustion efficiencies compared to coke. The gas-phase reactions appear to be influenced by the amount of volatile matter present in the carbonaceous matrix and its subsequent effect on the structural transformation of the particles because of the release of volatiles. The surface area of the coke–polymeric mixtures before and after combustion was found to be higher than the surface area of coke alone. The residual chars collected after the reaction in the DTF were characterized as a function of pore volumes and surface area of the particles. A previous study has demonstrated the possibility of partially replacing conventional coke in EAF steelmaking with end of life rubber tires. The present paper studies the potential replacement of MC with waste materials, such as PP and HDPE, as auxiliary fuels in EAF steelmaking. A comparison to previously reported combustion efficiencies for rubber blends is also provided.

Introduction

Steelmaking in an electric arc furnace (EAF) is based on the principle of subjecting scrap material to a high temperature (~1923 K) for about 45–50 min, until a molten bath is formed. With the aid of an electric arc, the gradual rise in temperature is assured. Normally, in an EAF, approximately 3.3 tons of lime or dolomite and 1.15 tons of carbon are added for every 100 tons of scrap.¹ Dependent upon the cost and availability, anthracite, metallurgical coke (MC), calcined petroleum coke, fluid coke, and natural/synthetic graphite are among the conventionally used carbon-based materials in EAF steelmaking.

About 550 kW of electricity is required to produce a ton of steel in an EAF, and thus, alternative routes striving to improve energy efficiency by providing further sources of chemical energy need to be considered. Different carbon-based materials could be used to partially replace the conventional materials. Plastics are composed of long polymeric chains, of C and H, which might supply energy when subjected to controlled high-temperature reactions. Above all, the ever increasing use of polymers poses serious problems in disposal, because of their poor biodegradable nature. The world annual consumption of plastics has almost reached 100 million tons; Australia only produces about 1.5 million tons of plastic waste per year, of which approximately 800 000 tons are landfilled.² Land filling

and incineration are the general practices of disposal, and these are becoming unattractive because of high greenhouse gas (GHG) emissions. Plastic materials contained in landfills emit harmful CO₂ and methane (CH₄) to the atmosphere upon decomposition.³ A serious concern is posed by CH₄ because its greenhouse warming potential is estimated to be 23 times greater than CO₂.⁴ Upon incineration of these waste materials, harmful emissions of volatile organic compounds, dioxins, and furans are exhausted if the process is not tightly controlled.⁵

The science governing the usage of plastic materials as a source of carbon and energy in the steelmaking industry is being extensively studied by our research group and has been reported earlier.^{6–8} Studies on the use of waste plastics in a commercial blast furnace and the raceway hot model at NKK Corporation have been reported by Asanuma.⁹ The combustion and gasification efficiency of the injected polymer particles were found to vary with the particle size. On the whole, the combustion performance was reported to be higher when plastics were involved. The combustibility of polyethylene

(3) Campbell, P. E.; McCahey, S.; Williams, B. C.; Beekes, M. L. *Energy Policy* **2000**, 28 (4), 223–229.

(4) Smith, K. A.; Ball, T.; Conen, F.; Dobbie, K. E.; Massheder, J.; Rey, A. *Eur. J. Soil Sci.* **2003**, 54 (4), 779–791.

(5) Li, C. T.; Zhuang, H. K.; Hsieh, L. T.; Lee, W. J. *Environ. Int.* **2001**, 27 (1), 61–67.

(6) Sahajwalla, V.; Rahman, M.; Khanna, R.; O’Kane, P.; Skidmore, C.; Knights, D. *Steel Res. Int.* **2009**, 80 (8), 531–539.

(7) Gupta, S.; Jacob, W.; Sahajwalla, V. *Energy Fuels* **2006**, 20, 2557–2563.

(8) Sahajwalla, V.; Khanna, R.; Zaharia, M.; Kongkarat, S.; Rahman, M.; Kim, B. C.; O’Kane, P.; Dicker, J.; Skidmore, C.; Knights, D. *Iron Steel Technol.* **2009**, 6 (43).

(9) Asanuma, M.; Ariyama, T.; Sato, M.; Murai, R.; Nonaka, T.; Okochi, I.; Tsukiji, H.; Nemoto, K. *ISIJ Int.* **2000**, 40, 244–251.

*To whom correspondence should be addressed. Telephone: 61-2-9385-7571. Fax: 61-2-9385-4292. E-mail: magda@unsw.edu.au.

(1) Ayed, P.; Clauzade, C.; Gros, B.; Huber, J.-C.; Lebrun, C.; Vassart, N. *Rev. Met. Paris* **2007**, 3, 128–135.

(2) Plastics and Chemicals Industries Association (PACIA). *National Plastics Recycling Survey*; Hyder Consulting Pty. Ltd.: Sydney, NSW, Australia, 2007.

(PE) was studied by Kim et al.¹⁰ with various experimental variables in a simulated blast furnace model. The energy efficiency was found to increase with the blast furnace temperature, oxygen enrichment, and smaller particle size. The simultaneous combustion of PE with coal was studied by Gupta et al.,⁷ proving not to pose any adverse effects on the combustion efficiency for pulverized coal injection applications.

The use of plastics as a partial fuel substitute for coke or coal in coke ovens and in the blast furnace is being practiced in Japan (JFE and NI), where the technology of plastic injection was designed through a unique integrating system.¹¹ Plastic injection has been developed by Bremer Stahlwerke in Germany, with more than 50 000 tons of plastic injected in their blast furnace.¹² Limited studies have reported the use of polymeric materials in EAF steelmaking,^{6,8,13,14} and they showed improvements in combustion performances and better carbon/slag interactions with the addition of plastics and rubber.

The usage of these waste materials in EAF steelmaking might bring advantages, on one side from the energy supply point of view and on the other side from their carbonaceous material applications for slag foaming. Given that polyolefins, such as PE and polypropylene (PP) are produced from petroleum, they are high-energy products with a calorific value of about 47 MJ/kg,¹⁵ which is equal or higher than most coals and cokes. Moreover, the residual mass from plastic/coke blends after gas-phase reactions is an important source of carbon, which can be further used for slag foaming in EAF steelmaking.^{6,8}

The combustion of most solid fuels involves two steps: thermal decomposition (pyrolysis) accompanied by physical and chemical changes and subsequent combustion of the solid residue. In the present paper, a thermogravimetric analyzer (TGA) was employed to study the effect of blending on the pyrolysis and combustion behavior of the carbon-based materials. The TGA provides change in sample weight against time, reflecting the thermal behavior (degradation) of the initial sample and the final residue. Because it was established that pore diffusion plays an important role in the kinetic regime of combustion reactions at the studied temperature,¹⁶ micropore surface area measurements were carried out for the blends before and after the reaction in the DTF, acquiring data on the opening of pores and their development during combustion, helping to establish the influence of plastic materials on their combustion efficiency.

In a drop tube furnace (DTF), the combustion efficiency is expressed in terms of carbon burnout as estimated on the basis of ash conservation. The same approach was applied in our previous study,¹⁴ when blends of coke and rubber were tested

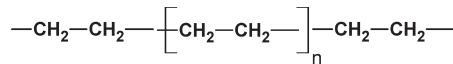


Figure 1. Molecular structure of HDPE plastic.

and their combustion efficiencies were estimated. Blends of varying proportions of MC with PP/high-density polyethylene (HDPE) plastics were tested in a DTF at a temperature of 1473 K under an O₂ and N₂ (20:80) gas mixture for studying the effects of the plastic concentration in the blend. The residence time of carbonaceous particles in a DTF is often of the order of seconds. These facilities are often used to compare the effect of fuel properties rather than taking a route of producing a complex complete simulation of the EAF conditions.⁷ The X-ray diffraction (XRD) technique and scanning electron microscopy (SEM) analysis are powerful analytical methods employed to understand the transformations taking place during the combustion of MC–plastic blends.

The present paper mainly targets the advantages brought about by replacing partially MC in EAF steelmaking with end of life products, such as waste plastic materials, and aims to determine the changes in combustion efficiency and associated structural transformations. We will also be comparing the present findings to those obtained in our previous study on blends of waste tires with coke.¹⁴

Effect of Plastic Chemical Structures. On the basis of their carbon content, plastics are ranked between coal and oil.¹⁷ Dependent upon the molecular arrangement and bond energies, plastic materials have different thermal decomposition behaviors.

PE is one of the most heavily used thermoplastic commodity in consumer products and is composed of a long chain of ethylene monomers with thousands of carbon atoms linked by single bonds (Figure 1). On the basis of density and branching characteristics, HDPE and low-density polyethylene (LDPE) are distinguished. While HDPE has little branching, LDPE is characterized by highly branched molecules, which are less tightly packed. Bond breakage in PE occurs in the molecular structure, producing small radicals accompanied by hydrogen release, which is favored over carbon monoxide release. The decomposition behavior of PE plastic was seen to be similar to that of coal.¹⁷ Thermal degradation is known to occur with random scission reactions, forming primary radicals.¹⁸ When oxygen participates in the thermal degradation reaction at a temperature of 773 K, the resultant products were hydrocarbons, with the number of carbons atoms ranging from C3 to C26, which represents a high content of olefins with terminal double bonds.¹⁹

The combustion study performed by Mitera and Michal¹⁹ in a flaming chamber showed that, on combustion at 873 K, PE released a great amount of products, which were further converted because of the oxidative atmosphere mostly to CO₂. Nonetheless, some stable, oxygen-containing compounds, such as pentanone, heptanone, and octanone, were found in the PE chromatograms. The combustion of PE at 1273 K primarily produces CO₂, with other products including α,ω -olefins, *n*-paraffins, and ketones, as well as aromatic

(10) Kim, D.; Shin, S.; Sohn, S.; Choi, J. *J. Hazard. Mater.* **2002**, *B94*, 213–222.

(11) Nishino, M. Recycling of waste plastics in Japan. Personal communication, 2000.

(12) Reinitzhuber, F. Waste plastic injection into the blast furnace, Bremer Stahlwerke. Personal communication, 2000.

(13) Zaharia, M.; Sahajwalla, V.; Khanna, R.; Koshy, P.; O’Kane, P. *ISIJ Int.* **2009**, in press.

(14) Zaharia, M.; Sahajwalla, V.; Kim, B. C.; Khanna, R.; O’Kane, P.; Dicker, J.; Skidmore, C.; Knights, D. *Energy Fuels* **2009**, *23*(1), 2467–2474.

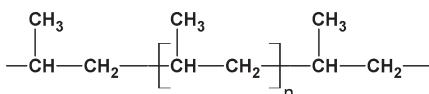
(15) Environment and Plastics Industry Council (EPIC). *A Review of the Options for the Thermal Treatment of Plastics*; EPIC: Mississauga, ON, Canada, 2004.

(16) Liming, L.; Sahajwalla, V.; Harris, D. *Energy Fuels* **2000**, *14*, 869–876.

(17) Kato, K.; Nomura, S.; Uematsu, H. *J. Mater. Cycles Waste Manage.* **2003**, *5* (2), 98–101.

(18) Faravelli, T.; Bozzano, G.; Colombo, M.; Ranzi, E.; Dente, M. *J. Anal. Appl. Pyrolysis* **2003**, *70* (2), 761–777.

(19) Mitera, J.; Michal, J. *Fire Mater.* **1985**, *9* (3), 111–116.

**Figure 2.** Molecular structure of PP plastic.

hydrocarbons, as a result of secondary aromatization reactions of the primary products. The above-mentioned products and the characteristic temperatures were also observed by other authors.^{20–23}

PP is a common thermoplastic consisting of a long chain of aliphatic hydrocarbons consisting of propylene monomers with a simple backbone and no bulky groups (Figure 2). They readily undergo a chain scission mechanism, giving highly reactive radicals, which are basically a source of carbon and hydrogen.

The thermal and thermo-oxidative degradation of PP has been studied by Michal et al.,²⁴ and they agreed on a similar behavior to that of PE. Besides, PP degradation was claimed to occur via a radical chain mechanism, which is simply the reverse of the polymerization reaction. The oxidative degradation of plastics was shown to form highly reactive free radicals upon the breakdown of C–C bonds. Thus, a radical chain initiates the degradation reaction, which then proceeds through propagation. After the combustion of PP, more oxygen-containing products were observed after reaching 873 K,²⁴ which are being composed of mostly branched methyl ethyl ketones (CH_3COR). Compounds of carbon atoms in multiples of three, from C3 to C15, are also prevalent following combustion. In any case, at higher temperatures (~1273 K), the availability of ketones is not pronounced and the presence of CO_2 and CO is greater. Thus, the PP chains are expected to oxidatively degrade, initially into smaller compounds possessing oxygen atoms in their backbone, which afterward break into simpler hydrocarbons.

PP and PE plastics may be regarded as supplementary fuel in EAF steelmaking because they have high calorific values and low moisture contents, while other beneficial properties include their high volatile matter (VM) and total carbon content.^{25,26} Therefore, it is critical to understand the combustion efficiency of these plastics when they are blended with coke, typically injected into EAF.

Experimental Section

Sample Selection and Preparation. PP and HDPE supplied by Orica, Sydney, Australia, represent the major constituents of plastic wastes. The conventional carbonaceous material used in this study is MC from the EAF at OneSteel Sydney Mill. Proximate (air dry basis, %) and ash analyses of the coke, plastics, and rubber (for comparison¹⁴) were carried out at Amdel Laboratories and Technical Services, NSW, based on

- (20) Hodgkin, J. H.; Galbraith, M. N.; Chong, Y. K. *J. Macromol. Sci.* **1982**, 17 (1), 35–44.
- (21) Piao, M.; Chu, S.; Zheng, M.; Xu, X. *Chemosphere* **1999**, 39 (9), 1497–1512.
- (22) Faravelli, T.; Bozzano, G.; Colombo, M.; Ranzi, E.; Dente, M. *J. Anal. Appl. Pyrolysis* **2003**, 70 (2), 761–777.
- (23) Font, R.; Aracil, I.; Fullana, A.; Conesa, J. A. *Chemosphere* **2004**, 57, 615–627.
- (24) Michal, J.; Mitera, J.; Tardon, S. *Fire Mater.* **1976**, 1, 160–168.
- (25) Alvarez, R.; Clemente, C.; Gomez-Limon, D.; Diaz-Bautista, M. A.; Mastral, A. M.; Callen, M. S.; Murillo, R.; Lopez, J. M. Proceedings of the 8th International Conference on Environmental Science and Technologies, Greece, 2003; p CD-1.
- (26) Zhou, L.; Wang, Y.; Huang, Q.; Cai, J. *Fuel Process. Technol.* **2006**, 87, 963–969.

Table 1. Proximate Analysis (Air Dry Basis, %) of the Starting Materials

	MC	PP	HDPE	rubber tire
moisture	4.9	0.01	0	0.9
ash	18.3	0.45	0.6	5.7
volatile matter	3.00	98.80	99.4	63.2
fixed carbon	73.8	0.74		30.2

Table 2. Ash Analysis of MC and Waste Rubber

ash analysis by X-ray fluorescence (XRF) (%)		
components	metallurgical coke	waste rubber tire
silicon as SiO_2	50.7	27.94
iron as Fe_2O_3	4.8	0.14
aluminum as Al_2O_3	36.0	3.13
calcium as CaO	3.3	8.38
magnesium as MgO	0.94	1.35
sodium as Na_2O	0.39	1.37
potassium as K_2O	0.53	0.05
phosphorus as P_2O_5	1.6	nd
sulfur as SO_3	0.39	7.58
titanium as TiO_2	1.4	nd
zinc as ZnO	nd	40.81

Australian Standard coal conditions and are provided in Tables 1 and 2.

MC samples were ground and sieved to a particle size in the range of 0.45–0.47 mm to minimize the effect of the particle size on the experimental results. PP and HDPE plastics arrived as pellets and were crushed in a specially designed plastic crusher (model Pulverisette 15, Fritsch GmbH, Idar-Oberstein, Germany) and sieved to particle sizes similar to those of the coke. The samples for the experiments were prepared by mixing MC and PP/HDPE particles in various proportions.

It can be observed from the analysis of coke and plastics that the highest amount of VM is present in HDPE and PP. Meanwhile, rubber embodies a high amount of VM, which is still much lower than that of the plastics. Volatiles are desired to certain extents for improved combustion, but a intense evolution of volatiles has been demonstrated to cause an endothermic effect, depleting the dense phase of oxygen and causing the formation of “hot spots”.²⁷ PP and PE exhibit a very high content of volatiles, and blending them with coke is expected to improve their combustion behavior to a certain extent.

Thermogravimetric Analysis. A custom-made TGA furnace was used to record the loss in weight of the carbonaceous blends during gas-phase reactions. The TGA consists of a mechanically movable vertical alumina tube furnace, a “Precisa” (1212 MSCS) analytical balance having a 1.2 kg capacity (1 mg accuracy) provided with a bottom-loading facility, a data logging computer, and a furnace. The temperature inside the high-temperature facility was controlled using a thermocouple external to the reaction tube, while the sample temperature was monitored through a thermocouple located under the sample holder inside the reaction tube. A schematic diagram of the furnace is presented in Figure 3, with Table 3 summarizing the operating conditions.

The samples were weighed and placed in a high-temperature-resistant sample holder, which was suspended in the sealed cold part of the analyzer. Weight loss was continuously recorded by a data logger connected to a balance and computer when the sample was heated from room temperature to 1423 K. The specimen was placed in the sample holder and held in the sealed cold zone of the furnace. The sample assembly containing blends of MC and PP was pushed into the hot zone when the furnace acquired the specified temperature. A mixture gas (20% O_2 and 80% N_2) was used for the combustion of PP blends under isothermal conditions. For the pyrolysis process, 100% N_2

- (27) Ogada, T.; Wether, J. *Fuel* **1996**, 75, 617–626.

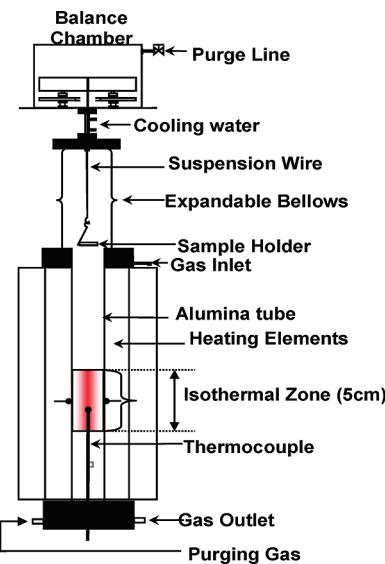


Figure 3. Sectional view of the TGA, with key features highlighted.

Table 3. Operating Parameters and Conditions Used in the TGA

operating parameters	values/condition
furnace	TGA
temperature (K)	1473
carbonaceous materials	metallurgical coke (OneSteel Ltd., Sydney, Australia)
types of organic material	PP and rubber
particle size (mm)	0.4–0.47
gas composition	20% O ₂ + 80% N ₂ and 100% N ₂
gas flow rate (L/min)	1.00
recording time (s)	every 5

was passed through the furnace. After the completion of combustion and pyrolysis reactions, the sample assembly was moved back to the cold zone before removing it.

DTF Tests. Blends of coke with PP/HDPE were injected through a screw feeder into a reaction zone, where the temperature was 1473 K. A Brook mass flowmeter controller adjusted the gas temperature, and the gas composition was maintained at 20% O₂ and 80% N₂. The schematic diagram and details of the vertical furnace are provided elsewhere.¹⁴ Residues of carbonaceous particles were collected at the bottom of the furnace after a 1–2 s residence time in the combustion atmosphere. A LECO analyzer measured the carbon content in the raw as well as residual samples, while a muffle furnace was employed to estimate the ash content of the feed and combusted char samples.

The combustion efficiency or burnout of the solid fuels (η) was calculated using the ash tracer method, often used for this purpose.^{7,28} The equation is given in our previous paper for calculation of the combustion efficiency of coke–rubber blends.¹⁴ In this study, the DTF burnout of MC is used to compare the effect of plastics (PP and HDPE)/coke properties on their combustion efficiency under the same environment.

Extensive literature reported lower temperatures for the breakdown of polymeric chains existent in PP and HDPE. Because the DTF provides a temperature much higher than the temperatures at which plastic decomposition occurs, the breakdown of polymeric chains is ensured and an improvement to a certain extent in the combustion performance for the plastic/coke mixture is to be expected.

Original and Char Sample Characterization. To explain the changes that occur during high-temperature gas-phase reactions

and the associated structural transformations in the particles, different techniques have been employed. XRD patterns of the materials in this study were acquired using a Siemens D5000 X-ray diffractometer. A thin layer of coke, PP, HDPE, and their corresponding blends was placed on a glass slide. Acetone was added to ensure particle adherence on the glassy support. After air drying, XRD spectra were obtained by scanning over an angular range of 10–50° (2θ), applying a step size of 0.02°, while acquiring scattering intensities at a rate of 0.5°/min when the accelerating voltage was set to 30 kV and 30 mA current. The micropore surface areas of the raw and reacted carbonaceous materials were measured using a Quantachrome micropore analyzer (NOVA 3200), available at UNSW laboratories.^{14,28} Using CO₂ as the absorbent and the Dubinin–Radushkevich (DR) method, the penetration of CO₂ into the micropore channels and the estimation of the corresponding surface area were ensured. When known sample weight and mercury were provided in the fixed volume penetrometer, pore volumes and bulk densities were estimated within an analytical range of 0.003–360 μm. The samples were placed on a tube and loaded into the degassing port of the apparatus, which was initially degassed at room temperature until a vacuum of 0.27 Pa was recorded. A heating mantle was then applied to the sample tube, and the contents were heated, under vacuum, to a temperature of 623 K. The sample was then left under vacuum overnight at a pressure of 0.27 Pa.²⁹ The porosimetry tests were conducted using a high-pressure mercury intrusion porosimeter (Micromeritics AutoPore IV) at Particle and Surface Sciences Laboratories, Gosford, Australia. Further investigation involving image analysis through the use of SEM was used to analyze the microstructure of the raw materials as well as the carbonaceous residues using a Hitachi S3400X scanning electron microscope operating at a voltage of 20 kV.

Results and Discussion

XRD Analysis. Structural changes developed by blending plastic materials with MC have been analyzed by XRD, and Figure 4 illustrates these patterns. Rubber and its blends with coke are also presented to highlight the differences in structural characteristics of rubber and plastic materials.

For the blend with coke and rubber, the position of the peak in the angular region (2θ = 10–35°) corresponds to the (002) carbon peak. The 100% raw PP sample exhibits a well-defined crystallinity because sharp peaks are predominant (Figure 4a) in the diffraction spectra. Four strong reflections are available in PP scattering intensities, (110), (040), (130), and (−131). The 100% HDPE reveals a predominant crystalline material because it is the linear form of PE (Figure 4b), while a strong (110) reflection peak arises followed by a lesser intensity (200) peak. However, these crystallized areas of plastic materials are unlike crystals found in graphite, because they do not have well-defined plane boundaries or sharp symmetrical edges. The existence of distinct humps that center at approximately 25° in the diffraction spectra of the raw rubber and its 30% blend with MC, as shown in Figure 4c, implies the presence of amorphous carbonaceous constituents in the matrices of the respective materials.³⁰ In the case of coke and rubber, the peak corresponds to amorphous carbon known to be characterized by a wide range of carbon lattice spacing. The amorphous carbon represents the disordered material and includes all of the non-aromatic carbon species.

(28) Kim, B.-C.; Sahajwalla, V.; Gupta, S.; Kim, S.-M. *Energy Fuels* **2008**, 22, 514–522.

(29) Rigby, S. P. *J. Colloid Interface Sci.* **2000**, 224 (2), 382–396.
(30) Kulaots, I.; Aarna, I.; Callejo, M.; Hurt, R. H.; Suuberg, E. M. *Proc. Combust. Inst.* **2002**, 29, 495–501.

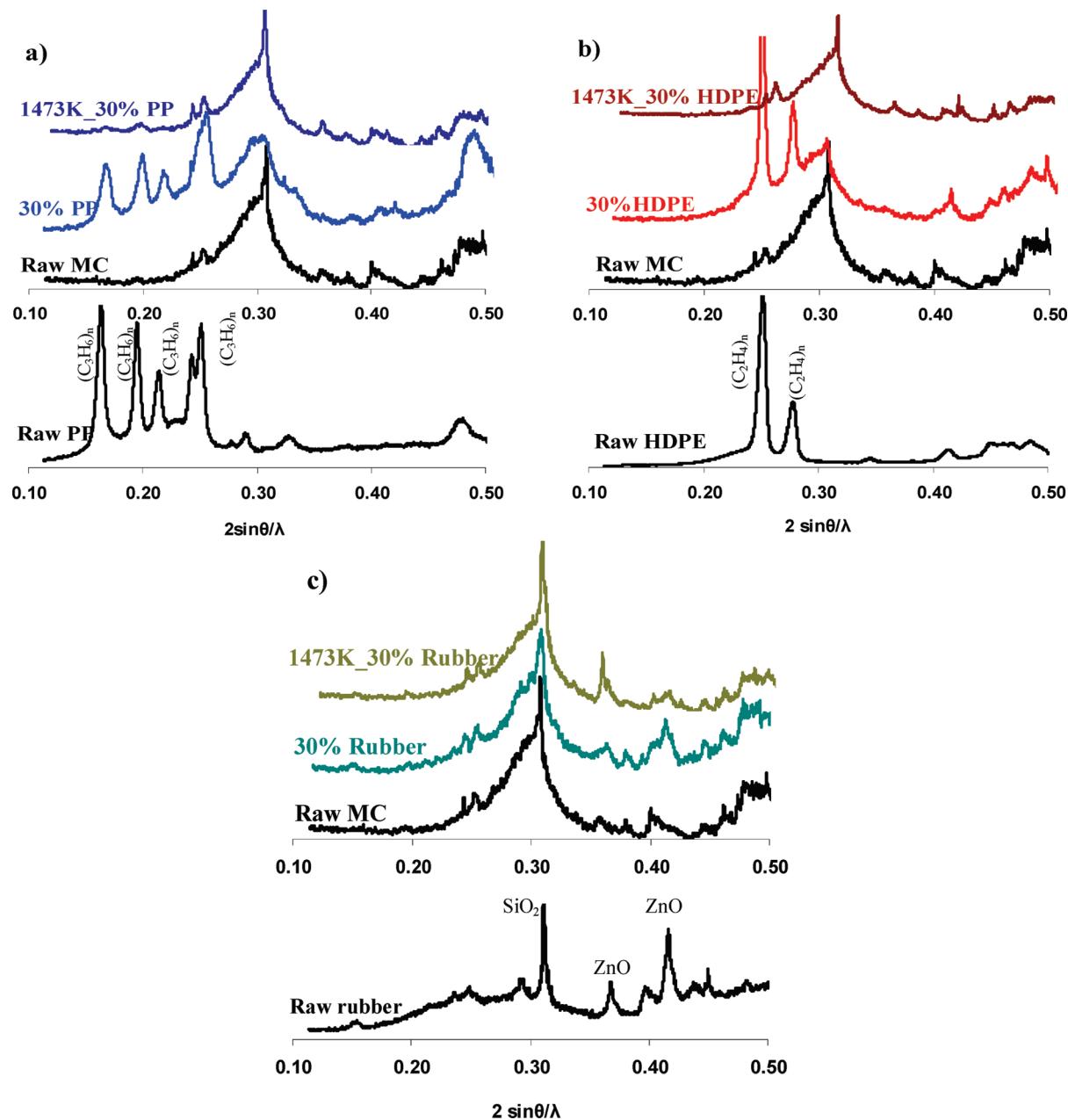


Figure 4. XRD patterns displaying peak intensities of raw coke and (a) raw PP and its 30% mixture with coke, (b) raw HDPE and its 30% mixture with coke, and (c) raw rubber and its 30% mixture with coke (for comparison).

The 30% PP and 30% HDPE blends showed characteristic peaks in the angular region of 10–25° because of polymeric inclusions with lower corresponding intensity peaks following the blending process. Because rubber and its coke blend revealed a highly amorphous appearance, a greater proportion of active carbon is situated at the carbon edges, which are expected to render better combustion efficiency over coke and the plastic mixtures.

The difference between rubber and plastic materials is a magnitude of the intermolecular forces and the capability of the individual chains to fit into a crystal lattice. The intermolecular forces between the long chains in PP and HDPE plastics have the tendency to align, creating a high degree of geometrical organization, while in rubber, they have the tendency to curl and fold, forming a highly disordered material. PE and PP are nonpolar polymers, and such materials are well-known for having weak intermolecular

forces between their chains, represented by van der Waals dispersion forces, which are also present between the rubber molecules.^{31,32} However, in rubber,³² the addition of sulfur resulted in a highly branched and cross-linked structure, increasing the strength of its intermolecular bonds. When these polymeric materials are subjected to combustion in the DTF, some of their end of chain molecules are broken, i.e., the intensive release of volatiles that might tear apart one chain from its neighboring molecule causing an intermolecular disruption, which might be significant if the bonds are weaker and the structure is simpler. Dependent upon the intensity of volatile release, structural transformations are seen throughout the samples,

(31) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley and Sons, Inc.: New York, 2006.

(32) Mark, H. *Ind. Eng. Chem.* **1942**, 34 (11), 1343–1348.

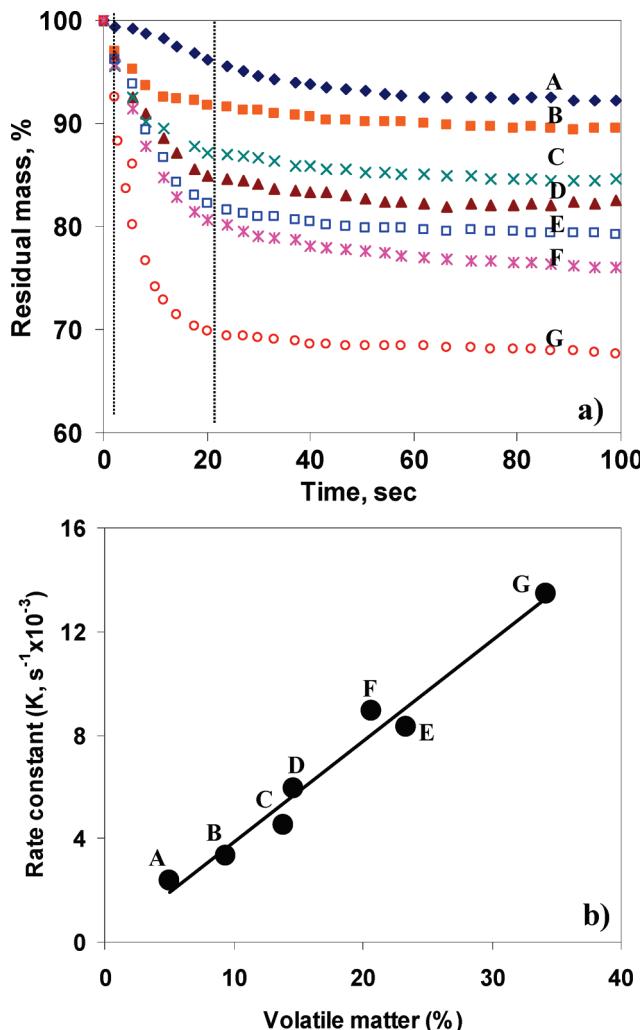


Figure 5. (a) Comparison of residual mass (%) curves of MC and its blends with PP and rubber at 1473 K and (b) variation of rate constants of the polymeric blends with VM at 1473 K in a N_2 atmosphere (A, 100% MC; B, 10% rubber; C, 10% PP; D, 20% rubber; E, 30% rubber; F, 20% PP; and G, 30% PP).

i.e., influence on porosity, surface area, and also, particle breakup. Experimental evidence to support such structural transformations is presented in a later section of the present paper.

Effect of Blending on Pyrolysis and Combustion. The characteristics of individual coke and plastic particles in the blend are expected to jointly influence the combustion behavior of the blends. As such, some properties of the blended materials were examined to analyze the characteristics of the blended materials that could affect the combustion behavior.

The combustion of carbonaceous materials encounters two stages: an initial sample pyrolysis stage, accompanied by VM removal in a high-temperature environment, followed by combustion of volatiles and subsequent heterogeneous reaction of the remaining char in the presence of oxygen.

The observed thermal behavior of coke and its blends with PP and rubber during pyrolysis in the N_2 atmosphere under isothermal conditions is shown in Figure 5. The intensity of volatile release can be quantitatively compared in terms of devolatilization rates,²⁸ which is calculated from the weight loss data by considering the first-order kinetics

Table 4. Type of Molecular Bonds and Bond Energies Required to Break the Fuels Considered in This Study^{32–34}

samples	bonds	bond energies (kJ/mol)
polypropylene (PP)	C–H	348
	C–C	413
polyethylene (PE)	C–H	410
	C–C	380
rubber (SBR)	C–C within aromatic ring	544
	CH ₃ –H	435
metallurgical coke (MC)	C=C	> 1000

using eq 1:

$$-\frac{dW}{dt} = K(W - W_\infty) \quad (1)$$

where W , W_∞ , and dW/dt are the initial mass of the sample, the final mass of the solid residue, and the rate of the mass change in a time range of 20 s, and K is the rate constant, in s^{-1} , respectively.

The total weight loss of MC and its blends with PP and rubber occurred in less than 100 s. Under the thermal effect, the maximum weight loss (%) observed in the TGA test was of the same order as reported in the proximate analysis (%) of the employed materials, i.e., 3% for MC, 18% for 10% PP blend, 25% for 20% PP blend, and 37% for 30% PP blend.

Figure 5a agrees that the high VM present in PP and rubber addition will result in rapid weight loss in a given time compared to coke. Correlating the rate constant of the tested samples with the actual amount of volatiles present in the initial blends (Figure 5b) reveals a linear increase in devolatilization rates with an increasing polymeric content in the blends. The rate constant of 20% PP is very similar to the rate constant developed by the 30% rubber blend, with a slightly higher value because of the overall amount of VM.

The rate of devolatilization appears to be faster for PP–coke blends compared to coke–rubber blends, while pure coke, as expected, shows the slowest rate. The striking difference is also attributed to the difference in the strength of the intra- and intermolecular potentials that contribute to the energetic forces present in the structure of the material. Within the molecule, the PP and PE plastics are linked together with relatively weak bonds, such as C–C and C–H bonds.³² Aromatic rings are present in the rubber molecule as styrene in the SBR backbone, assuring a more complex structure when compared to the tested plastics.³² As discussed earlier, the intermolecular forces in PP and PE are represented by weak van der Waals forces, while rubber is characterized by a three-dimensional framework following the vulcanizing process when sulfur was introduced and C–S and S–S bonds were formed. These cross-links introduced along the polymer chain are potential reactive sites for strong covalent bond formation.³¹

MC by its definition is comprised of a highly aromatic structure presenting a very immobile phase. Being derived from coal, which embodies mostly dense polycyclic aromatic hydrocarbons linked together by C=C(aromatic ring) bonds with a bond energy exceeding 1000 kJ/mol, MC develops an even higher resistance to heat following the coking process and VM removal. Besides, the lower amount of volatiles present in coke leads to a lower mass loss and little change in structure.

Table 4 summarizes the intramolecular bonds present in the samples used in the present study along with the corresponding energies required to break these bonds.

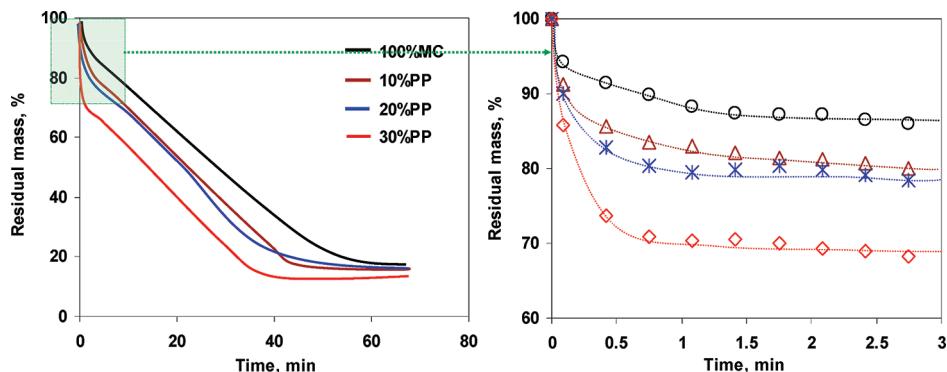


Figure 6. Comparison of the change in residual mass with time for 100% MC and its mixtures with PP at 1473 K combustion temperature in TGA.

The trends of the weight loss curves of HDPE and PP were seen to be very similar³⁵ because of chemical bonds in their molecular structure and an equivalent content of VM.

Tests in the nitrogen atmosphere at high temperature show that the weight loss derived mainly from volatile release, whereas combustion conditions lead to oxidation of VM and residual carbon, as shown in Figure 6.

Different behaviors are shown by coke and its corresponding PP blends, with larger fractions from PP being released as volatiles during the combustion process. This high amount of volatile yield was seen to occur over a relatively short time and is believed to influence the time required for complete combustion compared to MC.³⁶ The weight loss rate is faster for the 30% PP-coke blend, followed by the other PP blends, while 100% coke showed the lowest decomposition rate. On the basis of a high volatile yield of the blended materials, different authors^{28,37} have reported a similar behavior. The whole combustion reaction was spread over a long period of time. The initial stage of reaction, attributed to volatile oxidation (Figure 6b) took place over a relatively short time, on the order of seconds, followed by the combustion of the char spreading over 45 min. The remaining residual mass appears as a white powder and is believed to be ash.

To quantify the combustion performances of coke and its plastic blends, the extent of burnout in the DTF is estimated from the ash conversion equation used in our previous study¹⁴ and is presented in Figure 7 as a function of the polymer content in the blend at 1473 K and (20% O₂ + 80% N₂) gas concentration. It can be seen that both HDPE and PP blends developed higher burnout values than the parent coke.

An increase in burnout is observed with an increasing plastic content in the blend. Moreover, the combustion efficiency values of the two blends are similar. Considering the chemical and structural characteristics, i.e., amount of volatiles, crystalline structure, intermolecular bonds of PP and HDPE molecules, and weight loss curves, such a behavior is expected. In Figure 7, the burnout of rubber

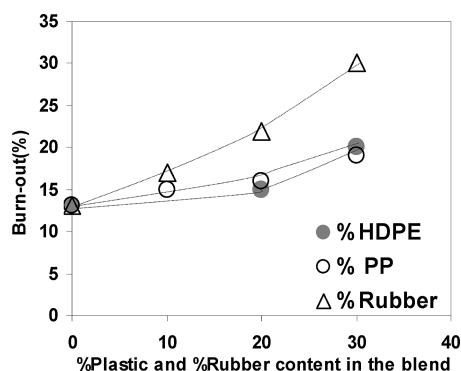


Figure 7. Effect of blending MC with varying PP and HDPE contents on the combustion of the blends at 1473 K in the presence of 20% O₂ + 80% N₂.

containing blends is also reported and compared to the burnout of PP and HDPE/coke blends. Higher combustion efficiencies are observed for the rubber blends. Our previous published paper¹⁴ presented the combustion efficiency values of rubber blends along with supporting evidence for such behavior. Detailed analysis of the species concerned are performed in the present study to explain the differences between the combustion efficiencies developed by rubber-containing blends and the combustion efficiencies developed by PP and HDPE/coke blends.

The presence of plastic materials has been reported to influence char properties in many ways. Gupta et al.⁷ conducted studies on coal/LLDPE and coal/HDPE mixtures and demonstrated an increase in the combustion efficiency at least up to the addition of 15% plastic. A further comparison of the burnout of the polymeric blends showed that the PE proportion in coal blends can be increased up to 30% without adversely affecting the burnout of the constituent coals. Related studies indicated a positive effect on the burnout by adding up to 20% plastic in a blend.^{38,39}

The amount of VM of the corresponding plastic blends influences the burnout values to a certain extent. Proximate analysis of the PP-coke and HDPE-coke blends suggests an increase in VM with higher plastic content in the blend (Figure 8a). An almost linear increase in burnout is observed

(33) Singh, B.; Sharma, N. *Polym. Degrad. Stab.* 2008, 93 (3), 561–584.

(34) Lin, J. P.; Chang, C. Y.; Wu, C. H. *J. Hazard. Mater.* 1998, 58, 227–236.

(35) Naruse, I.; Kameshima, T.; Omori, H. *Waste Manage. Jpn.* 2004, 145–154.

(36) Rudiger, H.; Greul, U.; Splithoff, H.; Hein, K. R. G. Final Report, APAS Clean Coal Technology Programme CT92-0001, 1995.

(37) Wang, C. L.; Leung, D. Y. C. *J. Anal. Appl. Pyrolysis* 1998, 45, 153–169.

(38) Goto, K.; Murai, R.; Murao, A.; Sato, M.; Asanuma, M.; Ariyama, T. Proceedings of the International Blast Furnace Lower Zone Symposium, Wollongong, Australia, Nov 25–27, 2002.

(39) Babich, A.; Gudenuau, H. W.; Senk, D.; Formoso, A.; Menendez, J. L.; Kochura, V. Proceedings of the International Blast Furnace Lower Zone Symposium, Wollongong, Australia, Nov 25–27, 2002; p 16.1.

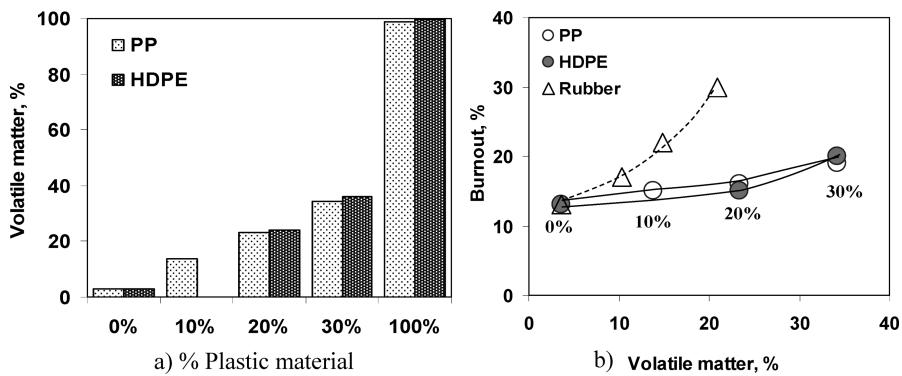


Figure 8. Effect of VM on the combustion performance of PP/HDPE–MC blends.

with a rise in VM, although the extent of burnout enhancement does not seem to depend upon only the amount of VM present in the carbonaceous mixtures (Figure 8b).

Higher combustion efficiency of coke/plastic mixtures could be significantly influenced by the quantity and nature of volatiles released during gas-phase reactions. The combustion efficiencies of both HDPE and PP blends can be explained in terms of the combustion behavior of the plastic particles. When unburnt plastic particles receive heat from the combustion of other already ignited particles in the vicinity, they tend to form gas phases and decompose rapidly. These gases would displace oxygen and form group flames (“puffs”).⁴⁰ Thus, for coke blends with HDPE and PP, the combustion of the constituents PE and PP would result in intense volatile release, creating local, oxygen-starved conditions that would prevent the complete combustion of neighboring coke and/or plastic particles. Overall, we are still seeing an increase in burnout (%) with the addition of a plastic proportion in the blend. Moreover, the devolatilization rates for PE and PP particles are greater, and this mechanism would also affect combustion,⁴¹ while rubber leads to lower rates of volatile release, affecting the structure over a longer period of time.

Effect of Physical Properties. It has been established that, at elevated temperatures and low residence times, as is the case of pulverized coal combustion, the reaction is likely limited by pore diffusion and possibly by chemical reaction on the pore surface.¹⁶ For such conditions, the physical parameters of the reacted materials play a very important role. Therefore, in the present work, the surface accessibility of coke and its blends with plastics has received increased attention and is assessed quantitatively through measurements of micropore surface area, pore size distribution, and pore volumes and qualitatively through SEM photomicrographs of the char particles collected after the oxidation reaction in the DTF.

In physical terms, CO₂ desorption is a phase equilibrium process, whereas mercury intrusion is a penetration process. In effect, the mercury intrusion curve measures the accessibility of the pore network, and it is expressed as the relationship between the intrusion volume and pore diameter, with the pore volume being mainly provided by macro- and mesopores.

Micropore surface area was measured for MC and its blends in different proportions with PP by pushing CO₂ in

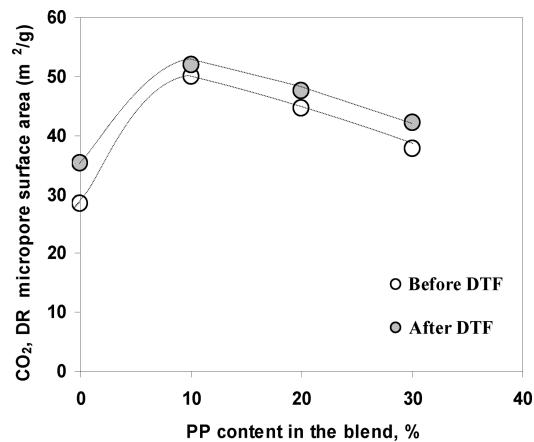


Figure 9. Changes in micropore surface area before and after combustion in DTF as a function of the plastic content in the blend.

the micropore channels, and a quantitative estimation is performed by applying the DR method. To explain the higher combustion efficiencies of coke/rubber blends over coke/plastic blends, the micropore pore surface area developed by coke/rubber blends is considered for comparison. Figure 9 illustrates the micropore surface area of the raw plastic-containing samples, which was found to increase when 10% PP replaced part of the coke. A further decrease was observed when the proportion of PP in the blend increased to 20 and 30% PP. The micropore surface area of coke/rubber blends was previously reported¹⁴ and was found to increase with an increasing rubber content in the blend.

To quantify the changes occurring during the reaction in a DTF, where oxidizing gas was present at 1473 K, micropore surface area tests have been performed on the collected residues. With char formation, an increase in surface area is expected.^{30,42} The tests demonstrated minor changes in the surface area for PP mixtures in the before and after reaction samples, i.e., from 49.9 to 52 m²/g for 10% PP, from 44.5 to 47.4 m²/g for 20% PP, and from 37.7 to 42.1 m²/g for 30% PP. Such an equilibrium can be reached when the mechanisms of pore enlargements and the opening of blocked channels are compensated by the coalescence of both micro- and mesopores as the carbonaceous material is consumed.⁴³

(40) Panagiotou, T.; Levendis, Y. *Combust. Sci. Technol.* **1998**, *137*, 121–147.

(41) Panagiotou, T.; Levendis, Y. *Combust. Sci. Technol.* **1996**, *112*, 117–140.

(42) Gale, T. K.; Fletcher, T. H.; Bartholomew, C. H. *Energy Fuels* **1995**, *9*, 513–524.

(43) Sahu, R.; Levendis, Y. A.; Flagan, R. C.; Gavalas, G. R. *Fuel* **1988**, *67* (2), 275–283.

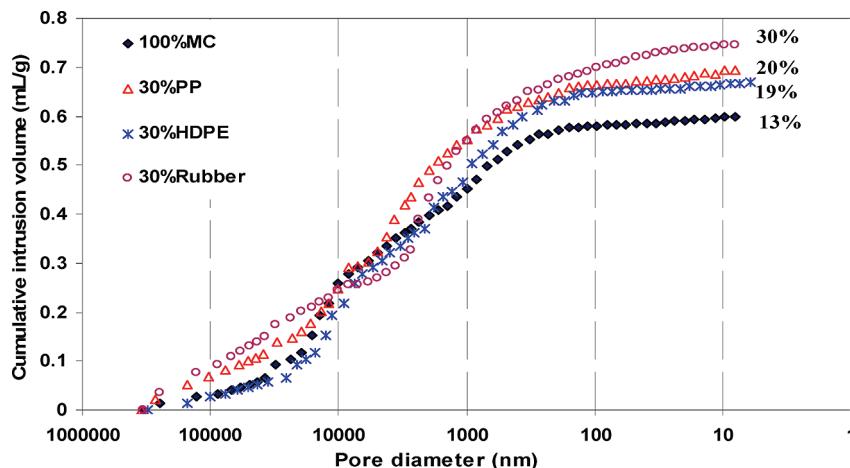


Figure 10. Effect of the cumulative intrusion volume and pore diameter on the combustion efficiency of coke and its blends with plastics and rubber.

Rubber presented well-defined differences in the before and after reaction samples with values from 35.4 to $45.6\text{ m}^2/\text{g}$ for 10% rubber, from 41.6 to $52.3\text{ m}^2/\text{g}$ for 20% rubber, and from 45.2 to $53.8\text{ m}^2/\text{g}$ for 30% rubber.¹⁴

There is a specific trend of change in the surface area. In the case of PP, the increase in area between before and after reaction samples increases with an increase in the percentage of the blend. However, in the case of rubber, this factor decreases with increase in the percentage of the blend.

The surface area in 10% PP blend is similar to the surface area in 30% rubber blend, yet the values of the combustion efficiency are not comparable. With rubber present in the carbonaceous blends, because of its amorphous structure, pores are being opened and the surface area is increased continuously. Intensive release of volatiles from the PP blends might cause particle breakup or coalescence of pores into larger ones, and thus, a drop in the surface area appears beyond 10% PP, which leads to lower combustion efficiency than that observed for rubber-containing blends. SEM analysis is required to support the above mechanism and is presented in the final section of this study.

Further on, Hg was pushed in the pore channels, and as a result, the characteristics of two kinds of pores are presented. Figures 10 and 11 illustrate the cumulative pore volume and total pore volumes of the meso- (partly) and macropores (cm^3/g) of coke and PP/HDPE/rubber blend residues collected after the reaction in DTF with a $(20\% \text{ O}_2 \text{ and } 80\% \text{ N}_2)$ gas atmosphere at 1473 K .

Mesopores have a diameter in the range of 0.001 – $0.02\text{ }\mu\text{m}$, while the macropores are greater than $0.02\text{ }\mu\text{m}$.

It can be seen from Figure 10 that the macropores of both chars developed by coke and its blends with plastic and rubber consistently take up most of the volume occupied by the residual particle. It is noteworthy that the mesopores also have notable contributions to the occupied pore volumes of the parent coke and the organic waste blends. The high porosity of the particles implies the existence of large amounts of feeder pores, comprised mainly of meso- and macropores.⁴⁴ The diameters of these pores are shown to be comparable to that of the mean free path of oxygen.⁴³

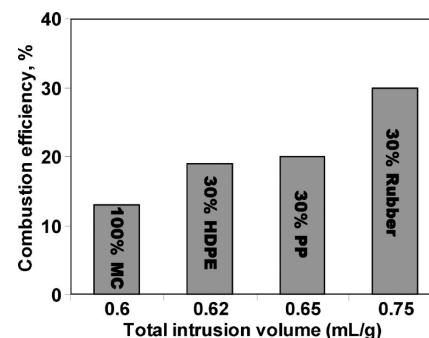


Figure 11. Total intrusion volume and the mass burnout magnitude of the four representative chars derived from MC and its blends with 30% PP, HDPE, and rubber collected after the reaction in DTF at 1473 K in $20\% \text{ O}_2$ and $80\% \text{ N}_2$.

These pores enable diffusion of oxygen into the active sites of the solid char matrix at high reaction temperatures and short residence times. Hence, a greater extent of porosity signifies higher oxygen reactivity of the solid particles.

The development of porosity in the residual chars seems to depend upon the amount of VM removed and the structural changes of the residual carbon. PP as a raw material has a high amount of VM. When in conjunction with the coke matrix, structural and physical changes might appear, because of the heat released by the combustion of polymeric volatiles.

The higher extent of porosity developed by the rubber blends over the PP blends might be due to the development of pores rather than simply particle fragmentation, which can occur because of the higher level of volatiles and their rapid release, as seen for PP (Figure 16a).

Figure 11 displays collectively the total pore volume (mL/g) of coke and its blended residues obtained from mercury porosimetry data and their combustion efficiency (%). Clearly, the extent of porosity, implied by the total pore volume (Figure 11) of the rubber blends, is the greatest, followed by PP and HDPE residues, while 100% coke is the lowest.

A good agreement between the extent of porosity (pore volumes) and that of burnout values of the polymer/coke blends is established in this study (see Figure 11). Similar correlations between physical parameters of the carbonaceous materials and their derived burnout were observed widely in

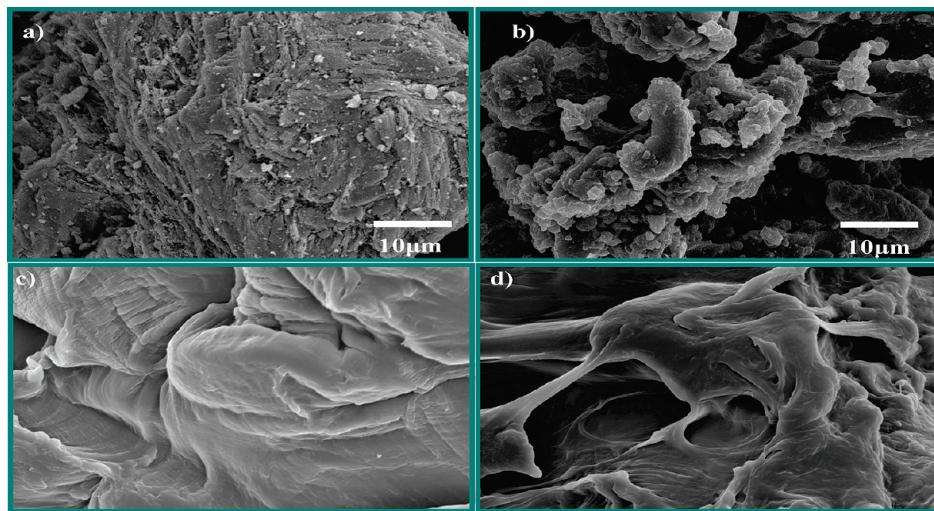


Figure 12. Morphological features of (a) 100% coke, (b) 100% rubber, (c) 100% HDPE, and (d) 100% PP before combustion in DTF at 1000 \times magnification.

the literature;^{43,45,46} however, these studies did not investigate coke/polymer blends.

For high VM content particles, increased temperatures and low residence times during combustion might lead to the formation of a high porous surface area and/or a liquid film layer on the outer surface of the particle. Such a liquid film might be responsible for the formation of some closed porosity in the char particles, and this is particularly common for thermoplastic materials.

The steps developed during the combustion of materials with a high volatile content in its composition, under diffusion control and possible chemically controlled conditions, are the following: (i) The blends are characterized by a certain amount of pores and associated gases (VM). (ii) Upon heating, the gas is detached and expelled via the pores, and in the case of thermoplastic materials, the carbonaceous matrix becomes plastic, leading to a reduction in the porosity. (iii) Cross-links are broken, forming solid residues and a high amount of gases. (iv) Gas is released that now opens some of the pores and/or leads to shattering of the particles, and the particles consequently develop more meso- and macropores.

When considering polymeric materials, evidence of bubble formation in polymers during thermal degradation was also found by Kashiwagi⁴⁷ in studies of piloted ignition of polystyrene. Using TGA and a rate of heating of 5 °C/min, they observed that bubbles are formed near the surface of the thermoplastic sample. Such a behavior is often observed for thermoplastic polymers as they soften and take on new shapes by the application of heat and pressure. We might assume that, during heating of the blends, the formation of bubbles and hence cavities within the plastic particles resulted in an increase in their surface area to a certain extent. This subsequently increased the contact area of the particles with oxygen and improved their combustion efficiency over coke.

However, it has been long recognized that, besides surface area, carbon active sites and catalytic inorganic impurities

d dictate the combustion performance of a carbonaceous material. Plastic materials used in this study are free of inorganic components, while rubber contains zinc oxide, silica, calcium carbonate, and some clay, while other inorganic compounds are present in low concentrations. These inorganic components are expected to be located at the edged sites of the carbon layer and at the vacancies between the carbon layers in the structure of the coke–rubber matrix.^{48,49} The presence of the inorganic components in the carbon active sites is perceived to catalytically enhance oxygen reactivity of neighboring carbon atoms in the carbon matrix through the number of possible mechanisms, depending upon species, chemical forms, and morphology of the constituent inorganic components. At high temperature, Ca is confirmed to be dominantly catalyzing for carbonaceous chars.

Some researchers^{50,51} suggested a possibility that, at high reaction temperatures, alkali earth metals catalyze the carbon oxidation reaction. Consequently, this catalytic reaction increases the particle temperature at the catalyzed sites, through the additional heat transferred to the particle surface from the oxidation of carbon and eventually the apparent combustion rates. However, Mitchell et al.⁵² found in her study that, for the particle temperature greater than 1500 K, the catalytic effect of mineral matter on the burning rate is negligible. This is likely associated with the sintering and agglomeration of mineral matters at high temperatures causing the loss of catalytic activity of mineral matter. The temperature used in our study is fairly close to the temperature used by Mitchell, and thus, the effect of the catalytic components in rubber is very limited.

Microstructural Changes in Coke–Polymer Blends. Panels a and b of Figure 12 present typical morphological features of 100% MC and 100% rubber reported earlier,¹⁴ along with 100% PP and 100% HDPE before combustion in DTF.

(45) Abd, El S.; Hampartsoumian, E. *Fuel* **1990**, *69*, 1029–1036.

(46) Wells, W. F.; Smoot, L. D. *Fuel* **1991**, *70* (3), 454–458.

(47) Kashiwagi, T. Proceedings of the 25th International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1994; pp 1423–1437.

(48) Mims, C. A.; Pabst, J. K. *Fuel* **1983**, *62* (2), 176–179.

(49) Laurendeau, N. M. *Prog. Energy Combust. Sci.* **1978**, *221*–270.

(50) Young, B. C.; Niksa, S. *Fuel* **1988**, *67* (2), 155–164.

(51) McCollor, D. P.; Sweeny, P. G.; Benson, S. H. Coal/Char Reactivity Final Technical Progress Report, Cooperative Agreement DE-FC21-86MC10637, 1987.

(52) Mitchell, R. E. Proceedings of the 23rd International Symposium on Combustion, The Combustion Institute, Pittsburgh, PA, 1990; pp 1297–1304.

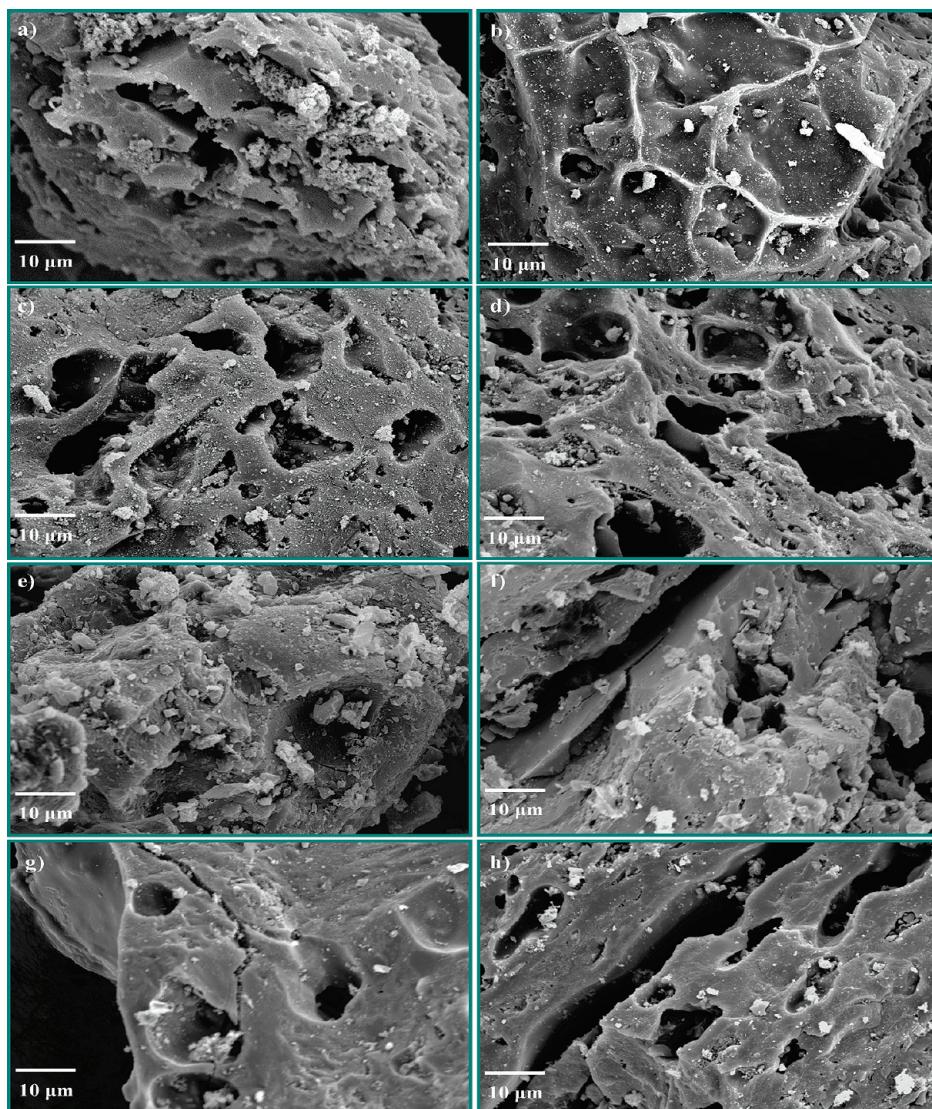


Figure 13. Morphological features developed after the reaction in DTF at 1473 K in an oxidizing atmosphere of (a and b) 100% coke, (c and d) 30% rubber, (e and f) 30% PP, and (g and h) 30% HDPE blends.

Several textural layers characterize coke samples with ash particles appearing as bright spots (Figure 12a). A rough surface with irregular shapes and more active sites, prone to participate in the combustion process, is distinguished within the rubber particle (Figure 12b). Plastic materials, on the other hand, illustrate very different morphological features; raw PP and HDPE seem to be very similar in appearance, displaying the same fluid and plasticized appearance (panels c and d of Figure 12).

With the occurrence of the reaction, the surface texture of the 30% PP–coke and 30% HDPE–coke residues becomes increasingly irregular because of changes in structure, which is caused by VM release (see panels e–h of Figure 13).

Release of the volatile material creates pores on the particle with rough surface and irregular features in the structures. Meanwhile, the possibility of fragmentation is apparent because several long cracks passing through the particle can be seen clearly and are attributed to the large amount of volatiles that are being removed from the carbonaceous matrix during the combustion reaction (panels f and h of Figure 13).

Also, the residue produced has a low density and is quite fragile, signifying a substantial attrition of the char. Rubber

displays a large amount of perforations throughout the particle, offering an increased number of paths for the gas phase to travel to access carbon (panels c and d of Figure 13).

The extent of porosity resulted from the combustion reaction is also illustrated in the SEM photomicrographs of the polished sections of coke (Figure 14), 30% rubber residue (Figure 15), and 30% PP residue (Figure 16) collected from the DTF at 1473 K in air. Large extents of perforations are visible at the particle surface of 30% rubber and 30% PP blend chars, while the residual coke exhibits a sharp edge and dense particle.

The morphology of the polished cross-section of 30% rubber residue revealed pores of different dimensions having clear round shapes (Figure 15), while 30% PP in the blend formed a large amount of pores quite different in appearance when compared to the pores in the rubber blend residue (Figure 16).

The conditions present in the DTF and the high volatile content in PP appear to help in developing a highly porous particle. On the outer surface, a liquid film layer is observed that discloses the approximate closed porosity of the char particle. Moreover, the photomicrograph in Figure 16a

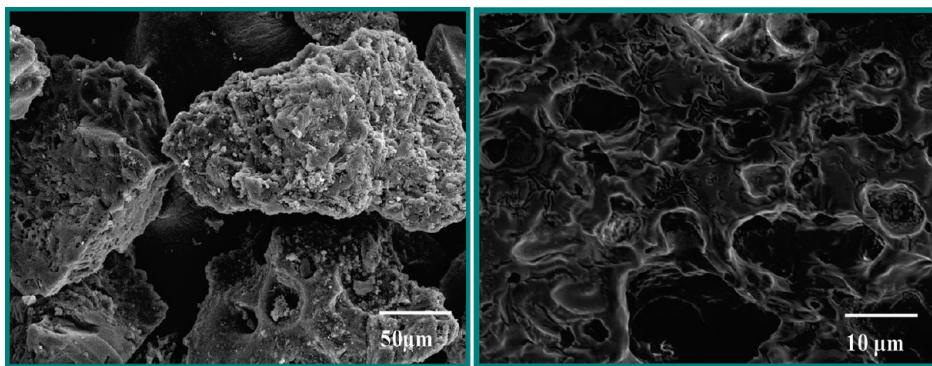


Figure 14. SEM micrographs of 100% MC collected after the reaction in the DTF at 1473 K in an air atmosphere: (a) entire residual particle and (b) polished section of the char particle.

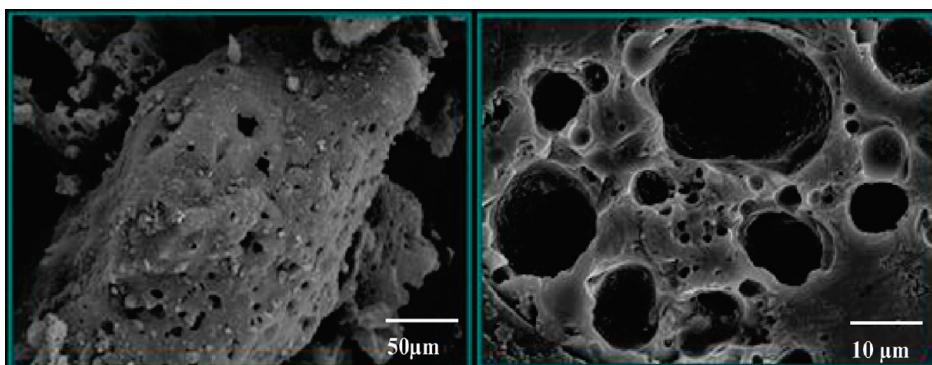


Figure 15. SEM micrographs of 30% rubber–coke blend collected after the reaction in the DTF at 1473 K in an air atmosphere: (a) entire residual particle and (b) polished section of the residual particle.

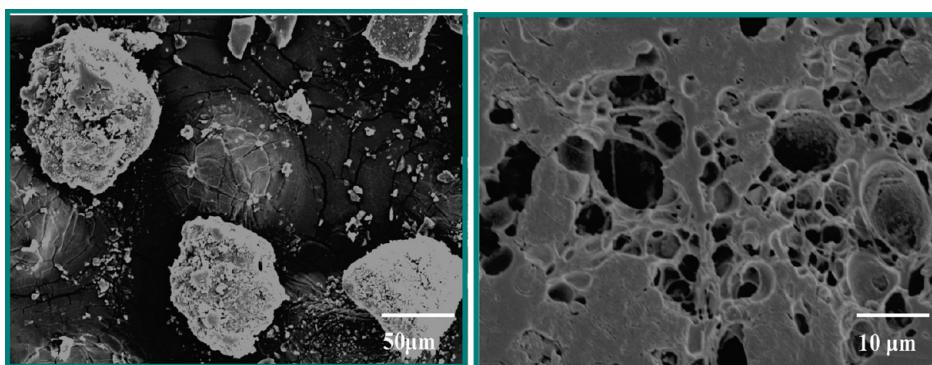


Figure 16. SEM micrographs of 30% PP–coke blend collected after the reaction in the DTF at 1473 K in an air atmosphere: (a) entire residual particle and (b) polished section of the char particle.

reveals the entire residual particle derived from 30% PP blend, and some shattered particles are also visible, which are attributed to the high devolatilization rates, resulting from the available volatiles in PP. The amount of VM in rubber-containing blends is released at lower rates when compared to the PP blends, thereby resulting in decreased residual particle shattering into smaller fragments but opening the existing porous matrix.

The distinctive morphological features of the blended residues resulted mainly from a much greater removal of volatiles present in the carbonaceous constituents of the macromolecular structure of rubber and PP compared to that of coke during combustion. When compared to coke, both rubber and PP have weaker macromolecular frameworks, with PP displaying the weakest structure as previously discussed in the

Effect of Blending on Pyrolysis and Combustion. Coke is one of the most complex carbonaceous materials, being comprised of three main phases, namely, carbon, pores, and minerals. All of these three phases are heterogeneous in nature. The evidence here and in a number of publications⁵³ is that the residual coke particle presents fine minerals intimately distributed in the carbon phase, residing close to the pores, while rubber and PP present a much lower amount of ash. This mineral distribution blocks the pores from further expansion, and thus, coke exhibits lower surface accessibility (porosity) than its blends with 30% polymeric materials.

(53) Gupta, S.; Dubikova, M.; Sahajwalla, V. Proceedings of the Association for Iron and Steel Technology (AISTech) 2006, Cleveland, OH, May 1–4, 2006; pp 19–30.

The morphology of the samples is consistent with the measured micropore surface area, pore volumes, and the calculated combustion efficiencies. The combined modifications of the pore and carbon structure of the residual char could be responsible for increased burnout values of the blends with increasing PP, HDPE, and rubber levels, i.e., as the polymeric proportion increased from 10 to 30%.

Conclusions

Combustion efficiency of coke and its blends in different proportions with PP and HDPE plastics have been investigated in this study with the aim of establishing the influence of volatiles and their release on structural transformations and combustion. (1) Increased combustion efficiency is observed with increasing plastic proportion in the blend; however, a comparison with rubber-containing blends reported in a previous paper does not support the role of volatiles as the only factor governing combustion. (2) The devolatilization rates were found to be in good agreement with the amount of volatiles present in the blended fuels. PP developed higher rates when compared to rubber blends, where the lower

devolatilization rates appear to affect the structure over a longer period of time. The difference in strength of the molecular structure of the materials is strongly connected to their kinetic behavior. (3) The effect on the structure of the particles, such as surface accessibility developed following gas-phase reactions in the DTF, also influences the combustion efficiency of coke–PP/HDPE and coke–rubber blends. (4) Good correlations were found between the extent of mass burnout of the blended residues and that of their pore volume, therefore supporting the dominant influence of the carbon surface accessibility (porosity) and blend components. The SEM photomicrographs illustrated a good agreement with the measured surface area, pore volumes, and their distribution in the carbonaceous matrix. (5) Combustion efficiency depends upon the amount of VM coupled with the rate of release of VM products and also the effect on the structure of the particles formed.

Acknowledgment. The authors thank Onesteel for their financial support. We also appreciate the technical assistance provided by Mr. N. Saha-Chaudhury and the help from Dr. Pramod Koshy.