

# ADVANCES IN THE RECYCLING OF PLASTIC WASTES FOR METALLURGICAL COKE PRODUCTION

M.A. Diez and R. Alvarez

Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080-Oviedo. Spain. e-mail: madiez@incar.csic.es

### Abstract

This paper is intended to provide useful knowledge on the use of plastic wastes for carbonization with coking blends in order to produce metallurgical coke. It focuses on the influence of the composition of plastic wastes on the pressure generated during the coking process and on the quality of the cokes produced in a semipilot coke oven. Several binary, ternary and multicomponent plastic mixtures of two types of thermoplastics, polyolefins (HDPE, LDPE and PP) and aromatic polymers (PS and PET) are used. It is shown that polyolefins may be employed to maintain the coke quality parameters but they have a negative effect on the generation of coking pressure, while plastics of the aromatic type such as PS and PET can be used to balance the generation of coking pressure. In light of the results, a relative proportion of polyolefins: aromatic polymers close to 65:35 w/w under the conditions applied in this study may be considered an optimum proportion for counteracting the generation of pressure during the coking process and for maintaining or enhancing the quality of the cokes. These results confirm previous findings using a different coal blend and multicomponent plastic wastes.

Keywords: Plastic wastes, recycling, coal, coking, metallurgical coke

### 1. Introduction

The environmental challenge of developing a recyclingoriented society requires the implementation and promotion of the law of the 3Rs (reduce, reuse and recycling) in order to minimize the environmental impact of wastes in landfill sites and to conserve our natural resources [1,2]. In recent years, the recycling of plastics from municipal wastes has increased via different routes including mechanical recovery, feedstock recycling and energy recovery. As a consequence, the amount of plastic household wastes dumped in landfill sites has decreased, but the amount of plastics disposed of in this way still continues to be a major problem and other alternatives need to be implemented. New strategies for recycling plastic wastes are of great importance, especially if they can be incorporated into consolidated industrial processes that offer a stable and continuous route. The feedstock recycling of plastic wastes in integrated steel industries could contribute to the expansion of plastic recycling via two routes: a) the blastfurnace where plastics are injected as a reducing agent [3,4]; and b) coke ovens as additives to coal blends for the production of coke [5-9]. Both recycling alternatives have been industrially implemented [3,5,6], where the local conditions and quality criteria allow it. In light of the different effect of each type of thermoplastics present in municipal wastes upon the properties of coal, the coking process and the coke quality [7-9], we have focused our attention on optimizing the relative proportion of two wellestablished plastic groups in the wastes: polyolefins (HDPE, LDPE and PP) and polyaromatics (PS and PET).

### 2. Materials and Methods

Co-carbonization tests of an industrial coal blend (B: VM= 23.9 wt% db, Gieseler fluidity = 517 ddpm), used by the steel industry in coke manufacture, with a plastic waste addition of 2 wt% (of both individual and mixed plastics) were carried out in a movable-wall coke-oven of 17 kg capacity. By means of this oven it is possible to measure the force exerted by the charge on the oven wall during the carbonization process (coking pressure) and to obtain a large enough quantity of coke for it to be characterized by the standard methods used by the steel industry. The plastic wastes were provided by the Spanish recycling company Abornasa. The bulk densities were kept in the 756±20 kg/m<sup>3</sup> range on a dry basis. The quality of the resultant cokes for use in a blast furnace was assessed in terms of reactivity to CO2 at 1100 °C for 2 h (CRI) and mechanical strength after reaction with CO<sub>2</sub> (CSR index) by the NSC method, following the ASTM D5341 standard procedure.

### 3. Results and Discussion

When HDPE is added to the coal blend at an addition rate of 2 wt%, the pressure generated during the coking process (Pc) increases from about 5 kPa in the case of the coal blend with no plastic waste added up to 39 kPa. This pressure value is extremely high and exceeds the safety limit established for cokemaking in this type of oven (maximum limit value of 20 kPa under the experimental conditions applied). A similar effect is observed for the binary mixture of LDPE and PP (37 kPa) and a muticomponent waste containing 95 % polyolefins (38 kPa). However, when PET is added to HDPE in different proportions (75:25, 65:35 50:50, 25:75) and to the LDPE+PP binary mixture (50:50), the coking pressure decreases until it reaches safe values. From these results, it is evident that there is a dependence between the percentage of total polyolefins in the waste and the coking pressure (Fig. 1), confirming that the increase in coking pressure is linked to polyolefins and that the relative proportion of polyolefins:polyaromatics in the waste is critical for obtaining safe blends for cokemaking. These results provide a useful basis for the optimization of the composition of plastic wastes for cokemaking in order to ensure that a force as low as possible is exerted on the wall during the process. On the basis of previous results [9], the maximum limit of 65 wt% was established as a safe quantity of polyolefins in a waste for ensuring a safe coking pressure.



Fig. 1. Relationship between the quantity of polyolefins in the waste and the coking pressure.

Before analyzing the coke quality parameters, it is important to point out that the values of the CRI and CSR of the cokes produced in the semipilot oven do not numerically match those obtained in industrial coke ovens. However, a comparison between cokes reveals differences that emerge as a consequence of the effect of the plastic wastes (Fig. 2).



Fig. 2. Variation of CRI and CSR of cokes produced from blends of coal and plastic wastes.

The reference coke B was produced from the coal blend at two different bulk densities, 802 and 761 kg/m<sup>3</sup> db. In general, although the plastic wastes added are different, the resulting cokes are quite similar, indicating that the reactivity to CO<sub>2</sub> (CRI) and the mechanical strength of the partially-gasified coke (CSR) are not greatly affected.

### 4. Conclusions

Although the coal blend characteristics, small variations in bulk density and heating rate may also have an effect on coking pressure, there is a clear relationship between the amount of polyolefins in the waste and the maximum permissible value of coking pressure. Some of the plastic mixtures tested may not give a realistic picture of municipal plastic wastes, but they nevertheless allow us to affirm that the optimum amount of polyolefins in a waste for ensuring optimal coking pressure and good quality is around 65 wt%.

#### Acknowledgements

The authors thank the European Commission for financial support in the RFCS Programme (Contract number: RFSR-CT-2005-00001) and the Spanish Ministry of Science and Innovation (project CTM2004-03254). We also thank Abornasa and Arcelor/Mittal in Spain for participating in the project

#### References

[1] Plastic Waste Management Institute, An Introduction to Plastic Recycling, Report 2009. Available at http://www.pwmi.or.jp

[2] Association of Plastics Manufacturers (APME). Plastics-the Facts 2010. An analysis of European plastic production, demand and recovery for 2009. Available at: http://www.plasticseurope.org.

[3] J. Janz and W. Weiss, Injection of waste plastics into the blast furnace of Stahlwerke Bremen, *Proc. 3rd European Cokemaking Cong.*, pp. 114-119, CRM-VDEh, Gent, Belgium, 1996.

[4] F. Hanrot, D. Sert, J. Delinchant, R. Pietruck, T. Bürgler, A. Babich, M. Fernández, R. Alvarez and M.A. Diez, CO<sub>2</sub> mitigation for steelmaking using charcoal and plastics wastes as reducing agents and secondary raw materials, In: A. López, F. Puertas, F.J. Alguacil and A. Guerrero., *Proc. 1st Spanish National Conf. on Advances in Materials Recycling and Eco–Energy. Recimat 09*, paper S05-4, Madrid, Spain, 12-13 November 2009. Available at: http://hdl.handle.net/10261/18433.

[5] S. Nomura and K. Kato, Basic study on separate charge of coal and waste plastics in coke oven chamber, *Fuel* 84 (2005) 429-434.

[6] S. Nomura and K. Kato, The effect of plastic size on coke quality and coking pressure in the co-carbonization of coal/plastic in coke oven, *Fuel* 85 (2006), 47-56.

[7] M.A. Diez, R. Alvarez, S. Melendi and C. Barriocanal, Feedstock recycling of plastic wastes/oil mixtures in cokemaking, *Fuel* 88 (2009) 1937-1944.

[8] S. Melendi, M.A. Diez R. Alvarez and C. Barriocanal, Plastic wastes, lube oils and carbochemical products as secondary feedstocks for blast-furnace coke production, *Fuel Processing Technology* 92 (2011) 471-478.

[9] S. Melendi, M.A. Diez R. Alvarez and C. Barriocanal, Relevance of the composition of municipal plastic wastes for metallurgical coke production, *Fuel* 90 (2011) 1431-1438.



# AUTO SHREDDER RESIDUE SEPARATION AND PYROLYSIS

<u>A. Santini<sup>1</sup></u>, Luciano Morselli<sup>1</sup>, Fabrizio Passarini<sup>1</sup>, Ivano Vassura<sup>1</sup>, David Serrano<sup>2,3</sup>, Javier Dufour<sup>2,3</sup>

<sup>1</sup> University of Bologna – Dept. Industrial Chemistry and Materials, viale Risorgimento 4, I-40136, Bologna, Italy.
<sup>2</sup> Department of Chemical and Energy Technology, ESCET, Universidad Rey Juan Carlos, c/Tulipán s/n, 28933 Móstoles, Madrid, Spain
<sup>3</sup> Instituto IMDEA Energy c/Tulipán s/n, 28933 Móstoles, Madrid, Spain

e-mail: ale.santini@unibo.it

## Abstract

This work deals with auto shredder residue (ASR or car fluff) refining since Directive 2000/53/EC claims for 85% material recycling from end-of-life vehicles (ELVs) in 2015. Plastics amount at about 10%by weight of modern cars and their use is likely to increase due to lightweight requirements and design freedom concerning colors and shapes. Current ELVs metal content is around 70% and with pretreatment 75% recycling rate can be easily achieved. ASR represents the remaining 25% ELV mass, and plastics are a rough 35% of the total car fluff. Plastics separation and recycling is thus strategic in order to meet ELVs Directive targets. In this work, floatation and sieving are used as ASR pretreatment. Pyrolysis of each obtained fraction has been carried on in order to evaluate which fraction is more suitable to feedstock recycling and whether pyrolysis could be used as recycling technique in ELV management. Results show that PP/PE mixture has highest conversion rate. Pyrolysis can be exploited to liberate metals and recover them from the char as well. Finally, if light plastics mix oil could be refined in a "waste to chemicals" optic, ELVs Directive targets can be achieved with pyrolysis.

Keywords: Auto shredder residue (ASR); pyrolysis; plastic separation; plastics recycling

### 1. Introduction

This work deals with auto shredder residue (ASR or *car fluff*) refining since Directive 2000/53/EC claims for 85% material recycling from end-of-life vehicles (ELVs) in 2015. Plastics amount at about 10% (by weight) of modern cars and their use is likely to increase due to lightweight requirements and design freedom concerning colors and shapes. Current ELVs metal content is around 70% and with pretreatment 75% recycling rate can be easily achieved. ASR represents the remaining 25% ELV mass, and polimers consist of little less than 50% of the total car fluff.



Fig. 1. Car fluff composition [1].

Plastics separation and recycling is thus strategic in order to meet ELVs Directive targets. In this work, floatation and sieving are used as ASR pretreatment. Pyrolysis of each obtained fraction has been carried on in order to evaluate which fraction is more suitable to feedstock recycling and whether pyrolysis could be used as recycling technique in ELV management

### 2. Materials and Methods

Two density stage floatation has been used to sort plastics from the non-organic matrix. The Pyrolysis reactor consists of a semi-continuous reactor provided with a helicoidal stirrer [2]. In a typical experiment, 10-15 grams of the chosen sample were loaded into the reactor. Products were collected as light and heavy oils in two coolers and gases in a Tedlar bag. Solid residue was recovered once the reactor cooled down as well and metal content weighted. Oils and gases were then analyzed with GC-MS to identify products. Authors decided to carry out also some runs using a nanocrystalline HZSM-5 zeolite catalyst placed in the reactor together with the plastic-rich samples.

### 3. Results and Discussion

Results show that PP/PE mixture has highest conversion rate. Pyrolysis can be exploited to liberate metals and recover them from the char as well. Moreover, catalyst enhanced cracking by cutting down hydrocarbons chains shorter, and producing more gases and lighter compounds in the oil. Finally, if light plastics mix oil could be refined in a "waste to chemicals" optic, ELVs Directive targets can be achieved with pyrolysis.

### 4. Conclusions

Catalytic refining of the pyrolysis oil (and gases) remains the bottleneck of the "waste-to-chemicals" recycling in Europe, as well as an interesting field to develop research. Although in industrial applications they are currently used for generating heat, gaseous products could be also refined and exploited as chemicals in order to enhance ELVs recycling rate.

## References

[1] Santini, A., Morselli, L., Passarini, F., Vassura, I., Di Carlo, S., Bonino F., End-of-Life Vehicles management: Italian material and energy recovery efficiency, Waste Management.

[2] Serrano, D.P, Aguado, J., Escola, J.M., Rodriguez, J.M., Morselli, L., Orsi, R., Thermal and catalytic cracking of a LDPE–EVA copolymer mixture, Journal of Analytical and Applied Pyrolysis, Volumes 68-69, August 2003, Pages 481-494.