1st Spanish National Conference on Advances in Materials Recycling and Eco – Energy
Madrid, 12-13 November 2009
S05-9

PLASTIC WASTES, LUBE OILS AND CARBOCHEMICAL PRODUCTS AS SECONDARY FEEDSTOCKS FOR BLAST-FURNACE COKE PRODUCTION

S. Melendi, C. Barriocanal, R. Alvarez and M.A. Diez

Instituto Nacional del Carbón (INCAR), CSIC, Apartado 73, 33080 Oviedo, Spain

Abstract

Plastic wastes, lube oils and coal-tar are evaluated, individually and combined, as additives to coal blends for the production of blast-furnace coke. The effects of adding 2 wt% of potential additives or their mixtures (50:50 w/w) on the coking capacity of coal, the pressure generated during the coking process and the coke quality parameters were evaluated. Using a combination of polyolefin waste and lubricating oil with high-boiling hydrocarbons has the beneficial effect of reducing the coking pressure generated by polyolefins without any significant deterioration in coke quality.

Keywords: Coal, Plastics, Oils, Coal-tar, co-carbonization, Thermoplasticity, Coking pressure, Blast-furnace coke

INTRODUCTION

In recent years, the recycling of plastics from municipal wastes and other post-consumer sectors has increased considerably. This is because landfill storage is considered a provisional situation rather than a rational solution for the problem of wastes. Mechanical recycling is the optimum recovery option for homogeneous and relatively clean plastic waste streams. However, for certain post-consumer plastics (unsorted, small pieces, light weight and dirty varieties) this option has technical limitations and, consequently, other means of recycling such as feedstock recycling and energy recovery must be considered [1]. The use of plastic waste as a substitute for coal in the steelmaking industry can be regarded as an eco-efficient alternative for solving the disposal of plastics and for recycling plastic wastes which are not easy to recycle by mechanical means. Integrated steel plants offer two routes for plastic waste recycling: (1) the injection of mixed plastic wastes into the blast furnace via the tuyeres, a process which involves replacing pulverized coal and coke as a reducing agent [2,3]; and (2) the incorporation of plastic wastes into coal blends as additives for metallurgical coke production [3-7]. The combination of these two routes in the steel industry, blast furnace and coking processes, has been demonstrated to be viable at industrial scale [5] and offers a route for improving energy recovery and feedstock recycling while providing economic, social and environmental benefits at the same time.

Previous results obtained at INCAR-CSIC have shown that the composition of plastic wastes and the coking conditions (i.e. bulk density of the charge) have a great effect on coking pressure and coke quality. Polyolefins, high- and low-density polyethylene (HDPE and LDPE) and polypropylene (PP) have a negative effect on coking pressure since they increase it to levels that can be considered as dangerous for the coke ovens [7]. To prevent this from occurring, different solutions have been proposed: applying a low bulk density of the charge which has a negative effect on the coke yield and quality; and adjusting the relative proportion of polyolefins and other plastics in the waste. Another possibility is to use other hydrocarbon sources in order to reduce the high level of viscosity of the melted plastics. In a recent study, it has been found that petroleum-based oils act as efficient solvents of the melted polyolefins and that they are able to reduce the coking pressure while the quality of the coke is maintained or even slightly improved [8].

This work explores the feasibility of mixing lube-oil wastes from steel plants and byproducts of coking plants with coal: plastics blends. For this purpose, the thermal behaviour of binary blends of plastics, oils and tars, the development of the fluidity of a coal blend, the generation of gas pressure during the coking process and the quality of the coke are investigated.

EXPERIMENTAL

A coking blend (B: 23.6 wt% db volatile matter; 8.9 wt% db ash; 0.57 wt% db sulphur; 352 ddpm Gieseler maximum fluidity) was used to prepare the mixtures with two plastic wastes (Pa and Pb), one coal-tar from the byproducts of a coking plant (Ta) and three oils -one synthetic oil (Q) and two mixtures of petroleum-based oil wastes (R and T)-, which are commonly generated at different stages of steel manufacture.

The plastic wastes were a three-component mixture Pa (70 % HDPE, 20 % PP, 5 % LDPE and 5 % PET) and a multicomponent waste Pb, mainly containing about 55 % of polyolefins and 35 % PET and PS.

Simultaneous thermogravimetric and differential thermal analyses (TG/DTA) of the plastics, oils and tar were carried out up to 600 °C at a rate of 10 °C/min in a nitrogen atmosphere.

Changes in the plasticity of the coal blend and its blends with the wastes were measured using a R.B. Automazione PL2000 Gieseler plastometer, following the ASTM D2639 standard procedure.

Co-carbonization tests were carried out in a semi-pilot movable wall oven of over 15 kg capacity to measure the wall coking pressure and to produce coke for the evaluation of mechanical and chemical properties. The coking time was nearly 3 h and the maximum temperature in the centre of the charge of 950 ºC. The amount of mixed plastic waste and oil added to the coking blend was 2 wt%. The quality of the resultant cokes with a view to their use in a blast furnace was assessed in terms of their reactivity to CO_2 at 1100 °C for 2 h (CRI) and the mechanical strength of the partially-gasified coke (CSR) was measured by the NSC method (ASTM D5341). The cold mechanical strength was evaluated on 10 kg of coke of >50 mm initial size employing a JIS drum. The DI150/15 index is defined as the amount of coke >15 mm, after a mechanical treatment of 150 revolutions (JIS K2151).

RESULTS AND DISCUSSION

The addition of plastic wastes to a coal blend with an initial fluidity of around 350 ddpm produces a decrease in Gieseler maximum fluidity. In agreement with previous results [4, 7-11], the extent of the fluidity reduction is dependent on the composition of the waste. The reduction was greater (60% vs. 50% of initial coal fluidity) when a waste containing a total amount of 35% of aromatic polymers (PET and PS) was added (Figure 1). The addition of oils and tars help to partially restore the fluidity loss caused by plastic waste addition and keeps the fluidity inside the optimum range (100-1000 ddpm) defined by the MOF diagram as coals giving a coke of acceptable quality for the blast furnace [12].

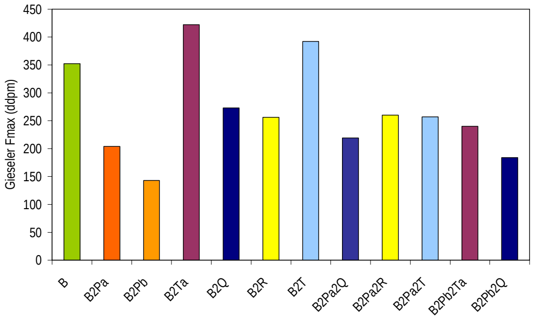

Figure 1. Variation of the Gieseler maximum fluidity of the coal blend with waste addition.

The additives selected (Ta, R, T and Q) differ in composition and thermal behaviour and, consequently, they influence coal fluidity in different ways. Tar (Ta) -a byproduct of the coking process and a raw material in carbochemistry- is composed of a complex mixture of aromatic hydrocarbons ranging from indene to benzoindene derivatives. It starts to distil at the beginning of the thermal treatment and shows a Tmax at relatively low temperature (274 ºC). Due to the compatibility of the aromatic hydrocarbons and the coal, the coking properties of the coal blend are enhanced. Oils R and T which contain long-chain aliphatic hydrocarbons behave differently [8]. While oil T presents a maximum evolution of hydrocarbons at 432 ºC, oil R contains lower-boiling hydrocarbons and maximum distillation occurs at 363 ºC. It seems that oil R which has a Tmax lower than that of the coal blend (485 ºC) is less effective in helping to maintain coal fluidity. Indeed, when this oil is added, fluidity loss amounts to for about 27 %. The synthetic oil Q, which is composed of high-boiling organic esters and is more thermally stable, with a maximum evolution of components (Tmax) at 446 ºC, has the effect of reducing the Fmax.

The force generated by the charge on coke oven walls during coking (coking pressure) can have a major impact on the life of conventional slot coke ovens. Excessive force can shorten oven life and cause operational difficulties during coke pushing. It is therefore necessary to keep the coking pressure below certain limits in order to prolong the life of the coke oven. All the additives were found to affect the coking pressure. The effects were defined as: negative (Pa) for unsafe pressure for coking (44 kPa); neutral (Pb and Ta) for no significant changes (around 20 kPa); and positive (Q, R and T) for a reduction in coking pressure to below 10 kPa (Figure 2).

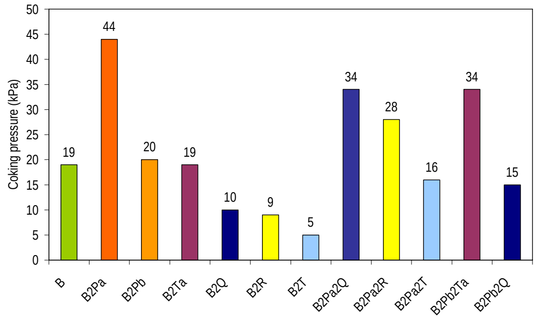

Figure 2. Variation of the coking pressure generated during coking with waste addition

Except for the Pb:tar mixture, the combination of plastic and oil in the blend has a positive effect in that it decreases the coking pressure. However, only oil T achieves safe values (< 20 kPa), and this occurs when the plastic waste is mainly composed of polyolefins.

Table 1 summarizes the quality parameters of the resulting cokes. By adding oil T to the mixture of coal blend B:plastic waste Pa, the coking pressure can be controlled without any significant negative effects for coke quality (mechanical strength –$DI_{150/15}$-, reactivity to CO_2 –CRI- and post-mechanical strength –CSR-).

Table 1. Bulk density of the charge and quality parameters of cokes produced from the coal blend with and without waste addition.

Blend	Db (kg/m^3 db)	DI150/15	CRI	CSR
B	795	77.8	28.9	61.1
B2Pa	795	76.9	28.2	65.0
B2Pb	795	77.2	30.9	61.0
B2Ta	793	75.5	27.3	63.4
B2Q	793	74.7	28.7	62.5
B2R	782	71.3	28.7	60.1
B2T	766	76.3	28.0	61.7
B2Pb2Ta	776	75.7	31.6	60.2
B2Pa2Q	793	75.8	30.0	63.5
B2Pb2Q	793	75.1	32.7	58.2
B2Pa2R	748	76.3	28.9	63.0
B2Pa2T	735	76.9	29.5	61.7

CONCLUSIONS

Of the petroleum- and coal-derived products tested for decreasing the coking pressure generated by polyolefins when these are blended with a coal blend, petroleum-based oils containing high-boiling hydrocarbons were found to be the most suitable. This type of oil does not cause any deterioration in coke quality.

ACKNOWLEDGEMENTS

The financial support provided by the Spanish Ministry of Education and Science through the research project CTM2004-03254 is gratefully acknowledged. We also thank Abornasa and Arcelor Mittal for providing the wastes used for this research. S. Melendi wishes to thank the Government of the Principado de Asturias –Spain- for the award of a predoctoral grant with funds from the PCTI-Asturias.

REFERENCES

[1] Association of Plastic Manufactures in Europe (APME). Annual Reports. http://www.apme.org

[2] Janz J, Weiss W, 1996. Injection of waste plastics into the blast furnace of Stahlwerke Bremen, p. 114-119. 3rd European Cokemaking Congress, CRM-VDEh, Gent, Belgium.

[3] Hanrot F, Sert D, Delinchant J, Pietruck R; Bürgler T, Babich A, Fernández M, Alvarez R, Diez MA (2009). CO_2 mitigation for steelmaking using charcoal and plastics wastes as reducing agents and secondary raw materials, *Proceedings. Recimat 09.*

[4] Diez MA, Alvarez R, Canga CS, Barriocanal C, Gayo F, Domínguez A, 2000. Co-carbonization of Coal with LDPE and HDPE Plastic Waste at Three Different Scales. p. 717-718. Ext. Abst. Eurocarbon Vol. II,

[5] Kato K, Nomura S, Uematsu H (2002) Development of waste plastics recycling process using coke ovens. *ISIJ Int. 42: S10.*

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

[7] Diez MA, Alvarez R, Barriocanal C, Melendi S, 2007. Possibilities of the coking process for the recycling of plastic wastes. Eurocoke Summit 2007, Intertech-Pira, Nice (France).

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

[9] Nomura S, Kato K, Nakagawa T, Komaki I. (2003). The effect of plastic addition on coal caking properties during carbonization. *Fuel 82, 1775-1782.*

[10] Sakurovs R (2003). Interactions between coking coals and plastic wastes during co-pyrolysis. *Fuel 82, 1911-1916.*

[11] Diez MA, Barriocanal C, Alvarez R, (2005). Plastic wastes as modifiers of the thermoplasticity of coal, *Energy and Fuels 19, 2304-2316.*

[12] Okuyama Y, Miyazu T, Sugimura H, Kumagai M (1970) Prediction of the coking property of coal by microscopic analysis*. J. Fuel Society of Japan 49 (522), 736-743.*