CO-COKING OF STAMPED CHARGES WITH THE WASTE ORGANIC ADMIXTURES

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ABSTRACT
By use of plastic or rubber admixtures in the stamped charges, it is possible to affect the properties of tar, in contrast to the calorific value of resulting coking gas; further, it was found that the reactivity- and strength parameters of the obtained blast-furnace coke are good or acceptable. Unused plastics or rubber can economize on part of the coal used in a stamped charge. Additions of both light and heavy plastics can be used up to 5 % of a charge weight; in the case of rubber it is not advisable to exceed 2 wt.-% in a charge. In contradiction to the other methods, which process the unused plastics of up to a content of 1 % in a charge, it is possible, in the case of used stamping method, to process even 2 % or more.

KEYWORDS: coke, co-coking, charge, plastics, rubber

1. INTRODUCTION

The coking of stamped charges with organic admixtures was carried out in the carbonizing test equipment of the Coke Oven Plant of Třinec Steel Works/Czech Republic under operational conditions. This equipment – KARBOTEST – allows the determination and prediction of the yield of coke and its quality, and the yield of by-products (Bartusek et al., 2002; Czudek, 2002). The content of plastics in charges was chosen to be 2–5 wt.-%, the content of rubber 2–3 wt.-%. These contents were chosen based on the conclusions from the laboratory experiments (Bičáková, 2002; Kříž et al., 2001, 2002, 2003) and taking into account the co-coking results in Japanese

works (Kato et al., 2002; Fukuda et al., 2003), which prefer small amounts of plastic admixtures in a charge. Three mixtures were examined as admixtures: a mixture of ABS polymer and rigid polystyrene; a mixture of polyethylene, polypropylene, polystyrene and cellulose/cellulose derivatives; and rubber.

2. EXPERIMENTAL

Coal and admixtures. The used coal was characterized by maceral analysis, coking properties, proximate analysis and the elemental composition of the coal substance. The parameters are summed up in Tables 1 and 2.

Table 1 Maceral analysis and coking properties of coal used. V, L, I–content in vitrinite, liptinite and inertinite (vol.-%), resp., R_{ov}–reflectance (%); SI–swelling index, a,b– parameters of Audibert-Arnu test (%), T_i (^{o}C), F_i (DDMP, DD)–fluidity parameters (constant-torque Gieseler metod, ASTM D 2639).

Maceral analysis				Coking properties							
V	L	I	R_{ov}	SI	A	b	$T_{softening}$	$T_{max.fluidity}$	$T_{solidification}$	F_{max}	F_{area}
65.2	3.6	31.2	1.10	5.5	29	51	422	454	484	585	4002

Table 2 Proximate and ultimate analysis of coal used (wt.-%).

W^a	A^d	S_t^d	VM^{daf}	C^{daf}	H^{daf}	N^{daf}	S_o^{daf}	O_d^{daf}
4.46	6.87	0.49	26.95	91.21	5.57	1.27	0.31	0.70

Table 3 The composition of the light plastics mixture (LDPE, HDPE–low-density and high- density polyethylene, resp., PP–polypropylene, FPS–foam polystyrene) (wt.-%).

METHOD	W^a	A^a	Cellulose	LDPE	HDPE	PP	FPS	Total
proximate analysis	0.5	3.2	96.3					100.0
TGA	0.5	6.7	8.1	84.7				100.0
DSC	-	-	-	1.6	16.6	65.6	4.4	-
hand sorting and DSC	0.5	4.1	8.1	1.6	15.0	66.3	4.4	100.0
considered contents	0.5	3.2	8.1	1.6	16.6	65.6	4.4	100.0

Table 4 Proximate and elemental analysis of rubber, the light plastics mixture, and mixture of rigid polystyrene (RPS) with ABS polymer (wt.-%).

ADMIXTURE	W^A	A^d	C^{daf}	H^{daf}	N^{daf}	S_o^{daf}	O_d^{daf}
rubber	0.93	11.78	85.59	7.65	0.57	1.04	5.14
light plastics	-	6.64	79.10	12.45	0.25	0.06	8.14
RPS-ABS	-	2.00	86.61	8.21	4.59	0.19	0.40

The composition of the light plastics mixture is shown in Table 3. The components in the mixture of light plastics were determined by a proximate analysis, differential scanning calorimetry (DSC) (on Perkin-Elmer DSC 7, 10 ºC/min), a thermogravimetric analysis (TGA) (on Perkin-Elmer TGA 6, 10 ºC/min), and in the cellulose share complemented by the determination by the wet chemical method (Zubková, 2003).

Another admixture was a mixture of polystyrene particles from rigid polystyrene (RPS) and ABS polymer in a weight ratio of 1:1, and rubber particles ranging in size 2–3 mm. The proximate and elemental analyses of admixtures are shown in Table 4.

The mentioned mixtures were composed based on the fact that a considerable part of the waste/unused plastics are polyolefines, especially polyethylene and polypropylene, and plastics from the electronics and electrical engineering industries (rigid polystyrene and ABS polymer). Also the rubber from tire-abrasion residue is a significant unused material, because the unused amounts are substantial.

Process conditions. The coking of stamped charges with admixtures was performed in a steel retort equipped with a temperature sensor in the center of a charge and another under an arch in the oven. The weight of a moisturized charge was 4000 g. A coking oven with electric heating and programmable heating regulators in the middle, lower and higher parts of the oven, and in the under-arch area enabled it to reach temperatures of up to 1000 ºC in the retort and a constant temperature of the resulting raw gas. The raw coking gas was vented into a water cooler for primary cooling and condensation of the raw water with some tar, and further into an electro-filter, where the remaining tar mist was eliminated. The total content of water in the liquid product was determined, as usual, by the xylene distillation method; the content of the reaction water was determined as a difference between the total content of water in the liquid product and the real content of water in the charge.

Charges containing 2–5 wt.-% of the plastic mixture or 2–3 wt.-% rubber were first moisturized into the final content of water 9 wt.-% and stamped, and then coked at an average heating rate of around 4 ºC/minute up to the final temperature of 930 ºC. The coking time was 4 hours. For comparison, a coal was also coked on its own under the same conditions. The

Table 5 Proximate analysis of charges (wt.-%).

Charge No.	Admixture	Admixture content	W_t^r (W^a)	A^d	VM^{daf}	S_t^d
coal	-	0	9.0 (4.46)	6.87	26.95	0.49
1	RPS-ABS (1:1)	2	9.0 (3.53)	7.48	26.27	0.57
2	RPS-ABS (1:1)	5	9.0 (4.38)	7.83	26.56	0.46
3	light plastics	2	9.0 (2.63)	7.67	27.02	0.48
4	light plastics	5	9.0 (4.51)	8.35	26.86	0.50
5	rubber	2	9.0 (4.03)	7.39	26.44	0.49
6	rubber	3	9.0 (3.81)	6.78	26.83	0.49

Table 6 The mass balance of coking and co-coking (wt.-%, dry).

Charge	Coke	Tar	Reaction water	Gas and losses
coal	75.8	3.7	2.3	18.2
1	75.6	5.2	2.8	16.4
2	74.2	2.6	3.5	19.7
3	75.0	2.4	3.4	19.2
4	73.4	3.4	2.6	20.6
5	76.7	2.9	1.6	18.8
6	77.1	4.5	0.5	17.9

grain size of the coal used was below 3 mm, of the plastics with a lower density under 2 mm, of the plastics with a higher density 3–4 mm, and rubber particles 2–3 mm. The density of the charges was 988 kg/m³ each time (recalculated to a dry charge). The proximate and elemental analyses of a coal charge and charges with admixtures are shown in Table 5. From the values in Table 5, it is obvious that the proximate parameters of the charges were practically constant, so the utility parameters of the products obtained will be determined chiefly by the characteristics of the admixtures chosen.

3. RESULTS

The mass balance of coking. The mass balance of coking and co-coking is shown in Table 6. With small amounts of the admixtures tested, it cannot be definitively said that the balance would move toward tar, water and gas at the expense of the main product – blast-furnace coke. Admixtures rather seem to change the products properties than the obtained amount, especially when tar and coke are concerned. Regarding gas, we may expect changes in the composition, but the crucial utility parameters –

calorific value and density – will change based on the amount of organic or plastic admixtures only slightly, because a change in the content of hydrogen and carbon monoxide, which are the most frequent, is compensated for by a change in methane content.

More substantial changes may be expected in tar properties, because synthetic polymers and their mixtures produce aromatic or aliphatic structures during pyrolysis, which can considerably influence both the chemical and physical properties of tar. The same also holds true for coke, because its reactivity and physical properties can be determined, apart from other things, by the ratio of aromatic and aliphatic/cyclanic structures in the initial mixture. Therefore, the utility properties of tar and coke must be tested very carefully.

The influence of admixtures on the properties of coking gas. The influence of the admixtures being considered on the composition and utility properties of gas was observed on the basis of the comparison of the composition, calorific value and density of the coke oven gas. The results are summed up by Tables 7 and 8.

Table 7 Composition of gas (vol.-%).

Gas	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	ΣC_4	N_2	O_2	CO	CO_2	H_2
coke oven gas	26.00		2.57				9.10	0.55	6.10	2.24	53.44
gas obtained	20.5-23	0.3-0.7	1.6-1.65	0.3-1.10	0.45	0.3-0.55	1-1.75	0	8-10	3-4	60-62

Table 8 Properties of gas (Q_s–calorific value, d–density).

Gas	Q_s (MJ/m^3)	d (kg/m^3)
coke oven gas	20.73	0.494
gas obtained	20.5 – 21.5	0.47 – 0.48

Table 9 Composition (wt.-%), density and FTIR-aromaticity index of tars obtained.

Charge	A[a]	H	C	N	S	O	Density (g/cm^3)	Aromaticity index (%)
coal	0.32	5.43	86.53	1.04	0.32	6.36	1.18	47.56
1	0.06	5.50	83.32	1.08	0.31	9.73	1.16	51.46
2	0.07	5.32	85.56	1.29	0.51	7.25	> 1.2	43.30
3	0.07	5.66	87.07	1.15	0.47	5.58	> 1.2	43.36
4	0.02	5.48	86.50	1.01	0.38	6.61	1.16	49.08
5	0.02	5.67	87.41	0.99	0.32	5.59	1.16	46.52
6	0.02	5.51	85.34	1.01	0.28	7.84	1.16	47.85

It is obvious from the values in Tables 7 and 8 that small amounts of the admixtures in question into charges will not influence the utility parameters of gas to a considerable degree, even though the differences in gas composition are evident. Coke oven gas contains more methane (26 % as against 20.5–23 %) but less hydrogen (53 % as compared with 60–62 %) and carbon monoxide (6 % in comparison with 8–10 %). These differences are created mainly by the presence of gaseous nitrogen (Table 7), but also by the character of hydrocarbons in the admixtures. In a number of the cases of laboratory co-coking of coal with synthetic polymers, biopolymers and organic admixtures, the calorific value of the obtained gas was higher than in the case of gas obtained from coking.

Properties of the tars obtained. Another important product of coking is tar, whose utility values can be influenced by the character and amount of the admixtures. Therefore the structure, density and aromaticity of the obtained tars were studied, while the aromaticity was expressed by the index of aromaticity calculated from the infrared spectra of tars. The infrared spectra were measured by FTIR spectrometer Nicolet 740 on a film on windows of NaCl with a sensitivity of 2 cm^{-1} using 32 spectrum accumulations (Central Laboratories of the Institute of Chemical Technology, Prague). The spectrum area of 3160–2750 cm^{-1} was divided by means of the mixed Gauss-Lorentz function into 9 bands – of which 3 bands belonged to the stretching vibrations of the aromatic C–H bonds and 6 to the aliphatic C–H stretching vibrations. From the ratio between aromatic intensities and the sum of aromatic and aliphatic bands, we have then calculated the index of the aromaticity of the tar being analyzed. The mentioned properties of the tars obtained are summed up in Table 9. From Table 9 it is evident that admixtures can principally influence the content of carbon (charge *1*) and the aromaticity of the resulting tars.

The decrease in the ash content in the tars from co-coking in comparison with the tar from the coal alone is striking. The various values of the aromaticity index show that an influence of even a small amount of plastic/rubber admixtures on tar properties is considerable. From the mentioned values, however, this influence cannot be specified, but it is obvious that an elucidation of the mechanisms of the reactions in question would bring a definitive evaluation of the influence of synthetic polymers on the structure and properties of tars resulting from co-coking.

Properties of cokes obtained. The key product of co-coking is a blast-furnace coke. In the cokes

Table 10 Proximate analysis, reactivity ($CRI_{Karbotest}$) and strength after the reaction ($CSR_{Karbotest}$) of cokes obtained.

Charge	Admixture	W_t^r (wt.-%)	A^d (wt.-%)	VM^{daf} (wt.-%)	S_t^d (wt.-%)	$CRI_{Karbotest}$ (%)	$CSR_{Karbotest}$ (%)
coal	-	0.1	9.4	0.89	0.47	41.2	50.5
1	HPS-ABS	0.1	9.3	0.64	0.48	41.4	50.8
2	HPS-ABS	0.1	9.2	0.73	0.48	41.6	51.1
3	light plastics	0.1	9.3	0.68	0.46	43.3	49.7
4	light plastics	0.1	9.4	0.53	0.53	45.4	45.1
5	rubber	0.1	10.2	0.74	0.48	45.5	41.6
6	rubber	0.1	10.2	1.14	0.47	48.2	38.0

Table 11 The rectified parameters CRI and CSR.

Charge	Admixture	CRI (%)	CSR (%)
coal	-	36.7	58.0
1	HPS-ABS	36.8	58.2
2	HPS-ABS	37.0	58.4
3	light plastics	38.2	57.5
4	light plastics	39.8	54.5
5	rubber	39.9	52.3
6	rubber	41.9	50.0

obtained, the decisive parameters were therefore observed using the standard method of Nippon Steel Comp., reactivity to CO_2 (CRI) and coke strength after the reaction with CO_2 (CSR). Also ash content, degasification and total sulfur in the cokes obtained were observed. The results are summed up in Table 10. It arises from the values in Table 10 that all of the cokes were well degassed (the values VM^{daf}), low-sulfur and low-ash.

The measured values of $CRI_{Karbotest}$ and $CSR_{Karbotest}$ were statistically converted to operational values based on long-term observations (Czudek, 2002). The rectified parameters are shown in Table 11. For the rectification the linear correlations were used.

It follows from the operational values of both parameters that it is possible to obtain quality blast furnace cokes by co-coking with plastics, because the CRI and CSR values for the coke from a coal alone and for the cokes from co-coking do not differ much. For if we – based on experience – consider the blast-furnace coke with the CRI value below 36 % to be of good quality and those with the values 36–40 % to be acceptable, then it would probably be only the coke with a mixture of 3 % rubber that would not be possible to use in a blast furnace on its own. It is similar with the CSR values: if we consider the cokes with a value above 57 % to be of good quality and with the values 52–57 % to be acceptable, then it would only be the coke from the mixture with 3 %

rubber again that could not be used as a blast-furnace one but e.g. for heating.

4.   CONCLUSION

By using plastic admixtures, it is possible to affect the properties of tar. Important is that the decrease in the ash content in the tars from co-coking in comparison with the tar from the coal alone is significant. The CSR and CRI parameters of a blast-furnace coke from co-coking are not substantially different in comparison with those of coke from usual coking, i.e., the unused plastics can economize on part of the coal used in a stamped charge. Additions of both light and heavy plastics can be used up to 5 % of a charge weight. On the other hand, a 3%-rubber addition influenced both parameters being considered. In view of the mentioned works of the Japanese authors, it can be estimated that in the case of rubber it is not advisable to exceed 2 wt.-% in a charge. In contradiction to the mentioned Japanese method, which processes the unused plastics of up to a content of 1 % in a charge, it is possible, in the case of used stamping method, to process even 2 % or more.

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