Co-pyrolysis of Waste Polymers with Coal

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Abstract: Co-pyrolysis of coal with waste polymers in a stationary quartz reactor was performed. Mass balance of the process was evaluated and properties of products were characterized. The main product (solid carbonaceous residue) exhibits low ash and sulfur contents and, from the point of view of application, satisfactory surface properties. Therefore, the solid residue is suitable as a smokeless fuel or as an industrial sorbent. The by-products were tar and gas. The tar may be used as a source of chemicals or a low-sulfur heating oil, the gas was highly calorific, therefore it may serve as a heating gas for energetical purposes.

INTRODUCTION

The increase in both production and consumption of polymers is accompanied by a rising occurrence of waste plastics in both industrial and municipal waste. Only a part of waste polymers can be recycled. Complex mixtures of polymers, especially with various other wastes cannot practically be recycled. Treatment of mixed municipal waste with high proportions of paper, cellulose, waste plastics, aluminium, and others is difficult. A way of coping with the problem is common pyrolysis of complex waste mixtures with coal (co-pyrolysis). Generally, co-pyrolysis of coal with organic admixtures gives useful gaseous, liquid and solid products. The solid carbonaceous residue (coke) can be used as a smokeless low-sulfur fuel or industrial sorbent[1,2]. Therefore, this method can be considered as one of the ways of treatment of non-recyclable waste polymers. Practically, there are three possibilities of co-pyrolysis of waste polymers with coal: high-temperature process with coal or with brown coal, and low-temperature co-pyrolysis with brown coal. We have investigated high-temperature co-pyrolysis with coal.

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EXPERIMENTAL

Materials

For the co-pyrolysis, coking coal from the Ostrava - Karviná mining district (Czech Republic) was chosen. The coal used contained 1 wt.-% of water and 2 wt.-% of mineral matter[5]. The total sulfur content was 0.7 wt.-%. Elemental analysis of the organic substance of coal is given in Table 1.

Table 1: Elemental analysis and minerals content of coal and model mixture of waste polymers (wt.-%)

Material	C	H	N	S[a]	O[b]	Ash
Coal[c]	84.3	5.1	1.2	0.6	6.9	1.9
Polymer waste mixture[c]	69.7	6.5	0.5	0.1	10.4	12.8

[a] Organic sulfur; [b] by difference; [c] dry

As waste polymers, a model mixture consisting of an epoxide resin, styrene-butadiene rubber and a mixture of polymers, paper, wood, rubber, glass, metals and minerals was used. Polymer components of the latter mixture were polystyrene (PS), polyethylene (PE), poly(ethylene terephthalate) (PET), polyurethane (PU) and poly(vinyl chloride) (PVC) (Table 2). Elemental composition of the waste mixture used and the ash contents are given in Table 1.

Table 2: Composition of model waste polymer mixture

Component	PS	PE	PET	PU	PVC	Paper	Wood	Rubber	Glass	Al[a]	Metals	Ash
Wt.-%	19	26	27	2	9	6	1	1	2	3	1	3

[a] Foil

Co-pyrolysis

660 ml (0.3-0.5 kg) of a mixture of coal with 15 or 30 % of waste polymers (grain size < 3 mm) was heated in a vertical quartz reactor in a tube electric furnace. The temperature during the co-pyrolysis rose slowly (5 °C/min) up to 900 °C. Tar and water were condensed in a condenser with a mixture ethanol - CO_2 (s) at -30 °C. Water was separated from the tar by azeotropic distillation with hexane. The gas obtained was collected. Tar was characterized by water and ash contents, density[3], elemental composition and by NMR[4]. Gas was analyzed by GC and also its density and calorific values were determined.

RESULTS AND DISCUSSION

The results of mass balance of co-pyrolysis are given in Table 3. All three types of admixtures caused a shift in the product yields from solid residue to volatiles (tar, water and gas). In the co-pyrolysis of coal with 30 % styrene-butadiene rubber, the increase in tar and reaction water is significant. In all cases, the yields of solid residue, tar and gas were satisfactory. The losses were acceptable; they were probably caused by an escape of the gas phase.

Table 3: Mass balance of co-pyrolysis (wt.-%)

No.	Mixture	Solid residue	Tar	Water	Gas	Loss
1	coal	70.6	9.2	5.4	9.5	5.3
2	coal + 15 % epoxide resin	64.4	14.0	6.7	10.9	4.1
3	coal + 30 % epoxide resin	57.9	20.2	7.0	11.0	3.8
4	coal + 15 % styrene-butadiene rubber	62.2	12.1	12.2	9.8	3.8
5	coal + 30 % styrene-butadiene rubber	56.3	17.4	15.3	8.7	2.3
6	coal + 15 % polymer waste mixture	64.8	10.2	10.5	10.4	4.1
7	coal + 30 % polymer waste mixture	58.2	12.6	14.6	10.7	3.9

The products of co-pyrolysis were characterized. The major product, the solid residue, was fine-grained; its physical properties and composition are presented in Table 4.

Table 4: Characteristic of solid residues from co-pyrolyses

No.[a]	Ash	C	H	S[b]	Porosity	S_{BET}	Q_s/Q_i
	wt.-%				%	m^2/g	MJ/kg
1	3.9	92.3	1.1	0.6	50.6	129	32.8/32.6
2	4.1	92.5	0.9	0.6	53.7	138	32.8/32.6
3	4.0	92.6	0.9	0.5	56.9	146	32.8/32.6
4	4.4	91.7	1.0	0.6	53.4	137	32.5/32.3
5	4.8	91.3	1.0	0.6	55.7	143	32.3/32.1
6	6.5	89.5	1.0	0.6	53.1	136	31.8/31.6
7	7.1	89.5	0.9	0.6	-	142	31.8/31.7

[a] See Table 3; [b] total

From the data it is clear that the solid residues obtained were well degassed (H content), with low ash and total sulfur contents. The waste additives caused an increase in the porosity of the solid residue from 50.6 % (blind) up to 56.9 %. From the point of view of its use as a smokeless fuel, the improvement in porosity is significant. The gross/net calorific values were satisfactory. The inner surface determined by the BET method was 136 - 142 m^2/g. Therefore, the use of the solid residue as an industrial sorbent can also be considered.

The evaluation of the tars obtained including aromaticity and substitution parameters is given in Table 5. Differences in the density (20 °C) of the tars were insignificant; in contrast, the addition of all admixtures reduced the sulfur content. From high aromaticity values, low ash contents and elemental composition, it is obvious that the tar may be used as a source for production of chemicals. Because its calorific value ranged from 35 to 40 MJ/kg, the tar from co-pyrolysis can serve as well as a low-sulfur heating oil as well.

Table 5: Characteristics of the tars from co-pyrolyses

No.[a]	Density g/cm^3	Ash	C	H	N	S[b]	O[c]	f_a[d]	σ[e]
		wt.-%							
1	1.02	0.2	84.1	7.7	1.4	0.4	6.4	0.69	0.48
2	1.04	0.1	80.1	7.6	1.0	0.2	11.0	0.71	0.33
3	1.07	0.1	78.7	7.2	0.8	0.2	13.2	0.79	0.26
4	1.02	0.2	84.9	7.9	1.4	0.3	5.4	0.68	0.25
5	1.02	0.2	85.5	7.9	1.9	0.2	4.5	0.71	0.19
6	1.00	0.3	83.0	7.5	0.9	0.3	8.1	0.65	0.37
7	1.00	0.3	82.5	7.8	1.4	0.3	8.0	0.67	0.31

[a] See Table 3; [b] organic sulfur; [c] by difference; [d] aromaticity (by NMR[3]); [e] substitution (by NMR[3])

The results of gas analyses are presented in Table 6. The addition of the oxygen-containing polymers (the epoxide resin and model waste polymer mixture) increased the oxygen content in the tar and the CO and CO_2 contents in the gas. All the three admixtures led to a decrease in the hydrogen content from about 64.9 to 58.8 vol.-% and to an increase in the methane content from 23.3 to 28.7 vol.-% as well as to an increase in the gaseous C2- C4 hydrocarbons. These changes in the chemical composition of gases led to a slight increase in the calorific value Q_s from 21 to 23 MJ/m^3. Therefore, the gas obtained can serve as an energetical gas.

Table 6: Composition (vol.-%) and calorific value of the gas from co-pyrolyses

No.[a]	H_2	CH_4	CO	CO_2	N_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	ΣC_4	Q_s MJ/m^3
1	64.9	23.3	5.6	1.7	1.1	0.3	1.9	0.2	0.6	0.4	21.1
2	58.0	26.3	7.4	3.9	0.6	0.4	2.0	0.4	0.6	0.4	22.0
3	58.8	22.6	9.1	5.2	1.1	0.4	1.8	0.4	0.4	0.4	20.4
4	57.8	28.3	6.6	1.8	1.5	0.4	2.1	0.3	0.6	0.5	22.8
5	58.1	27.4	7.2	1.5	1.4	0.6	2.2	0.4	0.6	0.5	22.9
6	56.3	28.7	7.2	2.5	1.4	0.5	2.1	0.2	0.5	0.4	22.7
7	58.6	26.1	7.3	3.0	1.2	0.6	2.0	0.3	0.5	0.5	22.0

[a] See Table 3

CONCLUSION

Co-pyrolysis of coal with polymers seems to be a suitable method of treatment of the mixed plastics waste. The products, gas, tar and solid carbonaceous residue, had suitable properties from the point of view of further applications. The fine-grained solid residue (coke) obtained exhibited low ash and sulfur contents, satisfactory porosity and an acceptable inner surface. Therefore, it can be considered as a smokeless fuel or industrial carbonaceous sorbent. The tar from co-pyrolysis had high contents of aromatics, low ash/sulfur contents, and high calorific value. The tar can be used as a source of chemicals or as a heating oil. The gas obtained can serve as an energetical gas.

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