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Kinetics of co-pyrolysis of high- and low-sulfur coal blends with additives

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Abstract

The thermogravimetric studies of a pyrolytic decomposition of blend based on low- and high-sulfur coals with additives (components of coal-tar and radical polymerization initiator) were carried out. Thermokinetic analysis demonstrated that thermal decomposition of the chemically treated bland proceeds more intensely than for the original bland and permits variation in the gas evolution rate on the different stages of pyrolysis process.

Keywords: sulfur coals, pyrolysis, kinetics

1. Introduction

Previous investigations indicate that the dependence of the coal structure and reactivity on sulfur content is fairly strong [1-2]. But there no a comparative data in the scientific literature about the thermal behaviour of low- and high-sulphur coals of the same rank in coking blends and in presents of additives. Developments of pretreatment methods for sulfur coals are especially desirable for reduction of the sulfur content in pyrolysis products and for the control of caking ability. The components of coal-tar and radical polymerization initiator are deemed as the most effective additives for cokemaking and for a study of the pyrolysis mechanisms [3]. The effectiveness of such materials at the different stages of pyrolysis process was compared.

The aim of this paper is a detailed study of the kinetic behaviour of low- and high-sulphur coals and their blend during pyrolysis with additives using thermogravimetry method and elucidation of usability of the thermokinetic analysis for coke properties determination.

2. Experimental

Experiments were conducted on the pairs of petrographically homogeneous low- and high-sulphur bituminous coals of Donets Basin. It was high-sulphur coal of J-Grade (J_{RC}: $C^{daf} = 87,3$; $V^{daf} = 31,7$; $S^d_t = 2,81$) and low-sulphur coal G-Grade (G_{LRC}: $C^{daf} = 85,1$; $V^{daf} = 36,0$; $S^d_t = 1,22$) according to Ukrainian classification and their blend (50:50). The samples were treated by radical polymerization initiator (acrylic acid dinitrile - AAD) and by the components of coal tar (pitch, anthracene, phenanthrene). The radical polymerization initiator was introduced to affect the course of radical reactions. Other additives were used as possible analogues of the

components, of liquid semi-coking and coking products which are known to be responsible for synthesis reactions during coking.

The thermal behaviour of coal blends were studied by thermogravimetric analyses and standard Sapozhnikov metods (GOST 1186-87). The thickness of plastic layer (y) and the contraction (x) by Sapozhnikov's method was applied as characteristic of coal coking ability. Derivatogrammes were registered in a Q-1500D derivatograph of Paulic- Paulic-Erdei system at the rate 10^0C/min in a closed platinum crucible under the layer of quartz sand up to 1000^0C. The kinetic parameters, i.e. the activation energy E and the rate of decomposition in different periods of pyrolysis were calculated by the results of the continuous measurement of the weight loss.

3. Results and discussion

Behaviour of the mass loss curves indicates that the blends decomposition process may be presented as a sum total of seven independent steps (linear parts on the curve TG). A Table 1, 2 shows the values of temperature intervals and corresponding mass loss for different steps of pyrolysis process.

Table 1 – The temperature intervals for independent steps of coals pyrolysis process.

Coals, blends (50:50)	Additive	The temperature intervals for different steps*, °C					
		I	III	IV	V	VI	VII
J_{RC}	–	100-140	350-415	415-480	480-595	595-867	867-930
G_{LRC}	–	75-125	327-400	400-472	472-504	504-573	573-894
$G_{LRC}+J_{RC}$	–	70-140	328-400	400-477	477-542	542-700	700-900
$G_{LRC}+J_{RC}$	AAD	75-180	350-420	420-455	455-530	530-757	757-900
$G_{LRC}+J_{RC}$	pitch	60-150	340-400	400-485	485-542	542-720	720-880
$G_{LRC}+J_{RC}$	anthracene	30-110	190-395	395-480	480-588	588-700	700-885
$G_{LRC}+J_{RC}$	phenanthrene	50-110	170-400	400-473	473-573	573-700	700-900

* II step is occurred without mass loss

It can be seen from the Table 2, that the most intensive decomposition of J_{RC} sample are occured at the IV-VI steps which is known to be related to formation of the main bulk of the semi-coking products.

The periods of the most intensive decomposition of G_{LRC} coal are the IV and VII steps. VII period (coking state) is characterized by a much higher rate of volatile products evolution from the solid phase as compared to the previous.

Thermal decomposition of blend is characterized by a comparative deceleration of the mass loss at the V, VI steps in comparison with J_{RC}.

Introduction of the radical polymerization initiator AAD results in acceleration of the gas evolution rate at the first - third steps (in a three or two-fold) and shift the temperature range of these stages to higher temperatures.

Таблиця 2 – Kinetic of the mass loss during independent steps of coals pyrolysis process, %.

Coals, blend (50:50)	Additive	Mass loss at different steps						$\Sigma\Delta m$
		I	III	IV	V	VI	VII	
1	2	3	4	5	6	7	8	9
J_{RC}	–	0,47	1,64	7,74	6,57	11,26	9,38	37,06
G_{LRC}	–	2,11	3,29	8,92	1,41	5,87	15,96	37,56
$G_{LRC}+J_{RC}$	–	1,88	1,88	8,45	5,16	7,04	10,79	35,43
$G_{LRC}+J_{RC}$	AAD	6,10	3,29	5,16	7,28	9,62	8,21	39,66
$G_{LRC}+J_{RC}$	pitch	1,88	2,35	8,92	5,16	11,97	9,39	39,66
$G_{LRC}+J_{RC}$	anthracene	2,81	3,99	8,45	7,74	4,92	10,32	38,23
$G_{LRC}+J_{RC}$	phenanthrene	2,35	5,16	7,74	6,81	5,40	10,33	37,79

There are reasons to believe that this acceleration appears due to scission of inter- and intramolecular bonds, including -C-S- bonds. This hypothesis is supported by the lowermost value for the activation energy for AAD-treated sample (Table 3). The removal of sulfur-and oxygen-containing groups causes a decrease in the rate of mass loss at the IV stage due to increases the thermostability of solid fuel. Decomposition rate increases at V and VI steps (semi-coking) and decreases during coking (VII period) under the action of AAD. This is indicative of the formation of more condensed structures by polyrecombination reactions.

Table 3 Thermokinetics parameters for the most intensive decomposition step in derivatograms of investigated coals and blends.

Coals, blends (50:50)	Additive	T_m, K[a], °C	(T_i-T_f)[b], °C	Δm, % at T_m	r[c] mg/(min ·g)	E_e, kJ/mol
J_{RC}	–	450	395-512	7,04	1,56	75,06
G_{LRC}	–	430	380-485	9,15	2,13	57,67
$G_{LRC}+J_{RC}$	–	440	380-495	8,45	1,92	67,58
$G_{LRC}+J_{RC}$	AAD	430	380-512	11,03	2,57	40,20
$G_{LRC}+J_{RC}$	pitch	450	390-505	8,92	1,98	54,66
$G_{LRC}+J_{RC}$	anthracene	440	400-505	10,79	2,45	42,29
$G_{LRC}+J_{RC}$	phenanthrene	440	395-512	11,26	2,56	40,81

[a] T_m - temperature of maximum reaction/process rate; [b] T_f - temperature of the final state, T_i - temperature of the initial state; [c] relative rate of thermal decomposition,

These data confirm that the addition of AAD to coal blend modifies the plastic layer: the thickness of plastic layer increases from 14.5 to 15.5 mm and the contraction increases

substantially from 27 up to 36 mm whereas the mechanical strength of coke is stable.

As can be seen from Table 3, the influence of all additives results in a decrease the values of E and a change the ratio of the rates of destruction and synthesis reactions. The influence of pitch is more pronounced only at the VI step. The rate of organic sulfur decomposition was highest in the same temperature range [4]. Moreover the total sulfur content in the obtained cokes was less than 1.5 %. There are reasons to believe that the pitch intensifies desulphurization process and improves of the coking ability of blends.

When anthracene and phenanthrene were added, an intensification of gas evolution processes at I, III and V stages and a significant deceleration of blend decomposition at VI stage are observed. The presence of these additives in the blend shifts the temperature region of the third stage to lower temperatures. Probably, highly condensed aromatic structures help to stabilize the free radicals present in reaction media with subsequent promotes of polyrecombination reactions at VI stage. Thermostability of linear structures is higher than angular. Therefore upon the effect of phenanthrene the conversion degree is increased from 1.88 to 5.16 at III stage. The reason for this is the lower value of the effective activation energy (E_e) in the process of vapour-gaseous products formation for phenanthrene in comparison with anthracene (depending on mutual arrangement of aromatic rings and variation in paramagnetic centers concentration).

Thus, treatment with AAD, anthracene and phenanthrene has exerted considerable effects. Thermo-chemical destruction promotes impoverishment of solid products with sulfur- and oxygen-containing groups, i.e. it improves their quality. These reactants act as radical polymerization initiators, thus increasing the yield of semi-coke (Table 3) and coke (Table 2) as compared to untreated blend. Accordingly, there are many grounds for believing that these methods of coal pre-treatment are a promising for low quality coals processing.

4. Conclusions

Chemical pretreatment has a considerable influence on the kinetics of co-pyrolysis of sulfur coal-containing blends. The use of additives (components of coal-tar and AAD) shows the possibility to manage of the rate and mechanism of the separate stages of pyrolysis process.

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