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Determination of material balance gasification of heavy coal tars with lignite and walnut shell

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Received August 5, 2019; Accepted November 3, 2020

Abstract

The reasons for the formation of heavy coal tars and the main directions of their processing and utilization are considered. The reasons for the formation of resinous products during gasification of low-grade raw materials are considered. The material balances gasification of materials: walnut shell (WS) and their mixture with heavy coal tars (WS+HCT), lignite (L) of the Alexandriya field (Ukraine) and their mixture with heavy coal tars (L+HCT) at their gasification were studied, namely: yield of solid residue, gaseous and condensed products and developed graphical dependences for each sample on air flow at a fixed temperature of 400 or 500°C. The component composition of condensed products for each experimental material is determined.

Keywords: Heavy coal tars; Lignite; Walnut shell; Gasification; Resinous products.

1. Introduction

Coal tar is one of the main and important products between others ^[1-6] of coke production. Heavy coal tars are also formed together with it, which are the result of the transfer of particles of the coking batch and the products of its thermochemical transformations with coke-oven gas ^[7-8]. Heavy coal tars are isolated from coal tar in mechanized clarifiers, as well as resin storages in the resin warehouse. The specific rate of formation is 0.5 kg/t of dry coking batch ^[9].

In ^[10-13] the main modern methods of disposing of heavy coal tars were presented, as well as the advantages and disadvantages of these methods were considered. Known works on the co-processing of solid fuel with heavy coal tars ^[14], the authors of which conducted research on the thermolysis of mixture of long-flame coal with coal tar or by-products of coke-plant (heavy coal tars, acidic tars, residues from the cleaning of coke-plant equipment and tar storage tanks, etc.) at a temperature of 673–1073 K. In order to obtain hydrocarbon residues thermolysis can be carried out in a fixed bed reactor, as described in ^[15]. Thus, it was found that the optimal amount of by-products of coke-plant in the mixture is 15 %, but its does not has a significant pore-forming effect. Hydrocarbon residues of high abrasion strength 88 % were obtained. Unfortunately, no information has been found on its gasification, although we believe that this type of organic processing is the most attractive for materials such as heavy coal tars.

Currently, in the world practice of gasification are subject, in addition to traditional fuels, such materials as: wood, solid waste, agricultural waste, liquid waste from pulp and paper production, used tires, etc. With the help of gasification not only problems related to energy supply are solved, but also problems of waste utilization.

Today, the issue of gasification of low-grade raw materials (biomass, municipal solid waste, etc.) is devoted to a sufficient number of works, for example ^[16-17]. One of the main problems that arise during_gasification is the formation of resinous products ^[18], the presence of which degrades the quality of the obtained gas (low calorific value), requires more efficient cleaning

before combustion, and others. In ^[19–28] proposals on tar cleaning depending ;on raw materials, reactor and its mode of operation, requirements for finished products, etc. are presented.

As published earlier ^[29-30], the Department of Oil, Gas and Solid Fuel Processing Technologies of National Technical University "Kharkiv polytechnic Institute" has developed a method of utilization of viscous organic coke-plant wastes to obtain generator gas, which includes lowtemperature gasification of a mixture of waste coke production with a solid carrier (namely, lignite or walnut shell) at a temperature of 400–500°C with the subsequent passage of the formed vapor-gas mixture through a layer of hot coke (800–1000°C).

The purpose of this study is to determine the material balance of the investigated materials in the area of gasification, namely: the yield of solid residue, gaseous and condensed products, to determine the quality of the condensed products.

2. Experimental part

2.1. Raw materials

Lignite (L) of the Alexandriya field (Ukraine), walnut shell (WS), heavy coal tars (HCT) of "ZAPORIZHKOKS", mixtures: 90 % (WL) + 10% (HCT) and 90% (L) +10 % (HCT) were used for research, the characteristics of which are presented in Table 1. Granulometric composition of experimental samples 3-5 mm.

Index			Tł					
		L	WS	НСТ	90 % (WS) + 10 % (HCT)	90 % (L) + 10 % (HCT)	Method	
PA	Wtr	9.40	7.60	1020	7.86	9.48	ISO 589:2008, IDT	
	Ad	39.80	2.30	3.90	2.46	36.21	ISO 1171-97	
	S ^d t	2.74	0.09	0.03	0.08	2.47	ISO 334-92	
	V ^{daf}	71.00	79.90	34.90	75.40	67.39	ISO 562:2010, IDT	
UA	C ^{daf}	67.56	52.52	94.09	56.68	70.21	ISO 625-96	
	H ^{daf}	6.95	5.98	4.28	5.81	6.68		
	N ^{daf}	0.89	0.19	1.29	0.30	0.93	ISO 333-83	
	O ^{daf}	21.86	41.22	0.31	37.13	19.71	ISO 1994-76	

Table 1. Characteristics of the raw materials

PA-Proximate analysis, %; UA-Ultimate analysis, %

2.2. Experimental equipment

The pyrolysis (low-temperature gasification) of prepared materials was carried out on laboratory equipment, which is the first stage of a two-stage laboratory installation for processing of viscous coke-plant wastes. The scheme of the equipment is presented in Fig. 1.

Principle of operation: the prepared material is loaded into a perforated vessel 1, which was placed at the bottom in the furnace 2, heated to a temperature of 400–500°C, fixing and temperature control of which is maintained through the control unit furnace 4. There, the oxidant-supply unit 5 serves oxidant-air. The products formed during destruction, representing a vapor and gaseous mixture, are sent through the connector 8 in the receiver-flask 6, that is cooled in ice water tank 7. The condensed products remained in the receiver-flask, and the gaseous ones were released into the atmosphere. At the end of the experiment, the condensation products were weighed together with the receiver-flask, the mass of which was determined by the difference between the masses of the receiver-flask before and after the experiment.



Fig. 1 Scheme of equipment for selection of condensed products

1 - perforated vessel; 2 -furnace; 3 - Chromel-Copel thermocouple; 4 – control unit of furnace; 5 – oxidant-supply unit; 6 – receiver-flask for condensation of products; 7 - ice water tank to cool the receiver-flask; 8 - the connector of the furnace and the receiver-flask; FI - flow meter

2.3. Experimental procedure

Conditions for the experiment: a portion weighing 20 ± 0.0001 g was introduced into the preheated furnace and kept for 40 minutes. During gasification furnace temperature was 400 or 500°C. The oxidant flow rate (V) fluctuated for WS and WS + HCT – 0.0005; 0.001 or 0.002 m^3 /min; for L and L + HCT - 0.002; 0.003 or 0.004 m^3 /min. At the end of the experiment, the cooled solid residue and condensed products were removed and weighed to an accuracy of ± 0.0001 a.

2.4. Method for characterization

Composition of condensed products was analyzed with GC-MS method. Conditions of analysis: gas chromatograph mas-spectrometer Shimadzu GCMS-QP2020; column - HP-5, 30 m \times 0.25 mm \times 0.25 µm; carrier gas – helium; initial temperature 60°C; isotherm – 1 min.; heating rate 20°C/min.; final temperature 260°C; duration of analysis 40 min; injection volume 1 µl; split 1:2; scan mode –TIC. Liquid samples were preliminary dissolved in diethyl ether (1:1000), filtrated and stored at 4-6°C.

3. Results and discussion

The results of determining the material balance are shown in Table 2.

able 2. The material balance of low-temperature gasification							
№ Raw m teria		The tem-	f The con- sumption of oxidant V, m ³ /min	Yield, %			
	Raw ma- terial	the fur- nace, °C		Solid resi- due, SR	Condensed products, CP	Gaseous products, GP	
1	2	3	4	5	6	7	
1		400	0.0005	18.21	22.13	59.66	
2	WS +		0.001	7.52	14.51	77.97	
3	пст		0.002	3.80	12.68	83.52	
4		400	0.0005	21.49	14.18	64.33	
5	WS		0.001	3.44	11.36	85.20	
6			0.002	1.48	6.47	92.05	
7	WS + HCT	S + 500 CT	0.0005	16.90	10.91	72.19	
8			0.001	3.15	8.86	87.99	
9			0.002	1.52	5.76	92.72	
10	WS	500	0.0005	15.30	10.20	74.50	
11			0.001	2.80	9.80	87.40	
12			0.002	1.28	5.52	93.20	

Nº	Raw ma- terial	The tem- perature of the fur- nace, °C	The con- sumption of oxidant V, m ³ /min	Yield, %			
				Solid resi- due, SR	Condensed products, CP	Gaseous products, GP	
13	L + HCT	500	0.002	38.36	2.64	59.00	
14			0.003	35.00	3.85	61.15	
15			0.004	25.50	9.49	64.01	
16			0.002	38.14	2.71	59.15	
17	L	500	0.003	34.28	3.78	61.94	
18			0.004	26.21	9.37	64.42	
19			0.002	39.59	2.14	58.27	
20	L + HCT	400	0.003	36.20	3.29	60.51	
21			0.004	28.20	8.75	63.05	
22			0.002	39.61	2.30	58.09	
23	1 L	400	0.003	36.34	3.41	60.25	
24			0.004	27.75	8.86	63.39	

The condensed vapor products obtained during processing are a mixture of many compounds. Since the number formed during the studies was insignificant (\pm 2 g and less), it was decided to collect complex samples for each raw material, the component composition of which was determined by chromato-mass spectrometry. The quantitative content of the components was estimated by the absolute normalization of the plane.

When determining the component composition of condensed products obtained after processing L, 52 compounds were identified (hereinafter-basic), after processing L+HCT 54 compounds were identified, after processing WS 75 compounds were identified and after processing WS+HCT 76 compounds were identified. Table 3 presents a list of the main identified compounds on the example of studies presented in ^[31–33].

Compounds	Raw material					
Compounds	WS	WS + HCT	L	L + HCT		
1	2	3	4	5		
phenol	24.50	26.43	4.44	8.14		
naphthalene	-	0.45	2.90	3.40		
butylated hydroxytoluene	2.14	7.89	7.96	11.28		
phenanthrene	2.44	1.17	2.65	2.63		
creosols	9.45	3.02	2.83	-		
fluorene	1.16	6.50	0.98	4.27		
pyrene	1.68	2.51	2.27	4.15		
heptadecane	1.09	1.13	1.84	2.04		
1-heptacosanol	0.24	0.22	8.16	7.14		
tetrapentacontane	0.36	-	5.81	6.13		
dotriacontane	0.35	-	2.55	3.47		

Table 3. Composition of condensed products, area %

From the data Tab. 2 it is seen that the formation of resin and resin-like compounds is influenced by the temperature of the furnace, air flow and the nature of the raw material. Therefore, in the gasification of WS and WS + HCT the formation of resin and resin-like compounds is greater than in the gasification of L and L + HCT. The higher the air flow and the higher the temperature of the furnace during gasification WS and WS + HCT, the lower the yield of condensed products. The higher the air flow rate and the higher the furnace temperature during gasification of L and L + HCT, the higher the yield of condensed products. In our opinion, this is due to the structure of the raw material and the temperature of the beginning of its destruction.

4. Conclusions

The material balances of the investigated materials (WS, WS+HCT, L, L+HCT) at gasification are determined, namely: yield of solid residue, gaseous and condensed products. The component composition of condensed products for each experimental material is determined. Developed graphical dependences of the yield of solid residue, gaseous or condensed products for each sample from the air flow rate at a fixed temperature of 400 or 500°C.

Symbols

- L lignite of the Alexandriya field (Ukraine);
- WS walnut shell;
- HCT heavy coal tars;
- *V* consumption of oxidant, m³/min;
- *W^r* moisture per working condition, %;
- A^d dry ash content, %;
- S_t^d total sulfur content, %;
- *V^{daf} yield of volatile substances to dry ashless state, %;*
- *C*^{*daf*} *carbon content in the dry ashless state, %;*
- H^{daf} hydrogen content in the dry ashless, %;
- *N*^{daf} nitrogen content in the dry ashless state, %;
- *O*^{*daf*} oxygen content in the dry ashless state, %;
- SR Solid residue, %;
- CP Condensed products, %;
- GP Gaseous products, %.

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