Low-temperature pyrolysis of coal with determination of physicochemical properties of coal and its thermal decomposition products

Nurken Nurgaliyev[1,3], *Aynagul* Kolpek[2], *Zhanar* Iskakova[1], *Sergey* Glazyrin[1], *Ruslan* Safarov[2], and *Yelaman* Aibuldinov[1]

[1]L.N. Gumilyov Eurasian National University, Research Institute of New Chemical Technologies, Astana, Kazakhstan
[2]L.N. Gumilyov Eurasian National University, Faculty of Natural Sciences, Department of Chemistry, Astana, Kazakhstan
[3]K. Kulazhanov Kazakh University of Technology and Business, Astana, Kazakhstan

Abstract. In the article the low-temperature pyrolysis of Kazakhstan low-grade coal with determination of physical and chemical properties of coal and products of its thermal decomposition is carried out. Elemental analysis of coal and analysis of mineral part of coal were carried out. 6 parallel experiments of the process of low-temperature pyrolysis of coal were carried out, as a result of which the yields of such products as semi-coke, tar, combustible gas were determined, and also their main characteristics (component composition, calorific value, etc.) were determined. The convergence of the results (from 6 experiments) is quite satisfactory. The heat balance of coal pyrolysis was carried out taking into account the average yields of products.

1 Introduction

Fuel and energy resources are the backbone of Kazakhstan's economy, among which oil, coal and gas are particularly prominent. Kazakhstan is among the top 10 countries in terms of proven coal reserves (about 2,4% of world reserves), where 2/3 is lignite and 1/3 is hard coal.

Being a valuable combustible fossil, coal remains the world leader in its use in the fuel and energy complex and is used to produce metallurgical coke, tar, carbon materials, humic acids, raw materials for the chemical industry (benzene, toluene, xylene, etc.) [1–3]. High-value liquid and gaseous fuels are extracted from coal with full utilisation of the structure and reactivity of coal [4,5].

For efficient utilisation of coal, it is important to understand the structure of coal. The organic structure of coal is generally considered to be a complex polymer with a high degree of cross-linking, including aromatic and aliphatic components [6,7]. There are significant differences in the organic structure of coals of different degrees of metamorphism, as well as obvious differences in industrial applications [8]. A thorough knowledge of the structure of coal with different degrees of metamorphism is necessary for the efficient utilisation of coal resources.

At present, among the existing methods of thermal processing of coal, pyrolysis is the most promising and investigated thermal treatment of such wastes as low-grade coals, oil sludge, etc. [9]. Pyrolysis is a common stage of many processes such as combustion, liquefaction, carbonisation, gasification, which usually operate in close systems in inert, reducing or oxidising atmospheres at different pressures and residence times [10]. Among the valuable products (derived from coal), coal tar is the main product of pyrolysis and can be used as an important raw material to produce olefins, value-added aromatic compounds, and coal tar based materials [11–14].

The purpose of this work is to study the process of low-temperature pyrolysis of low-grade coal of the Saryadyr deposit (Kazakhstan) with the determination of physical and chemical properties of coal and products of its thermal decomposition.

2 Research methodology

An analytical sample was prepared to analyse the initial coal. To evaluate the chemical composition of coal ash, a sample of 10 grams was prepared.

To carry out the process of low-temperature pyrolysis of coal, a 0,6 kg analytical sample of coal was preliminarily collected and an average sample was prepared for the pyrolysis process in a Fischer retort. The coal was air dried until an approximate equilibrium between the moisture content of the sample and the surrounding atmosphere was reached. The coal sample was gently pulverised so that at least 90% of it passed through a sieve with a 1 mm opening and no more than 50% through a 0,2 mm sieve. The prepared sample was stored in a hermetically sealed container. A suspension of charcoal (50 g) was heated in an aluminium retort to 520 °C for 80 minutes according to the heating regime given in Table 1. The decomposition products were directed to a receiver cooled with ice water. The resin and water were condensed. The gaseous products were discharged into the atmosphere after sampling for analysis. Determination of the component composition of the gas obtained as a result of coal pyrolysis was carried out on a LHM-8 MD chromatograph.

Table 1. Heating mode of the coal suspension.

Time from start of heating min.	Temperature, ^{0}C
10	220
20	310
30	380
40	440
50	480
60	505
70	520
80	520

3 Results and their discussion

3.1 Characterisation of initial coal

The results of analyses of initial coal are presented in Table 2.

Table 2. Characterisation of raw coal.

Properties	Conditional designation	Indicators per weight, %		
		analytical	dry	combustible
Mass fraction of moisture	W	4,00	-	-
Mass fraction of ash	A	30,06	31,31	-
Volatile substances	V	21,48	22,38	-
Elemental composition:				
Carbon	C	55,95	58,29	84,85
Hydrogen	H	5,35	5,57	8,11
Total sulphur	S	0,45	0,47	0,68
Oxygen	O	3,19	3,03	4,84
Nitrogen	N	1,00	1,04	1,52
Heat of combustion, lower	$Q_н$	5752,81, kcal/kg		
Heat of combustion, highest	$Q_в$	5776,81, kcal/kg		

The analysis of the mass fraction of chlorine and arsenic showed the following values: Cl – 0,043%, As – 0,0025%. The obtained indicators correspond to "traces" and are not further taken into account.

3.2 Characterisation of coal ash

The chemical composition of the mineral part of coal is presented in Table 3.

Table 3. Chemical composition of the mineral part of coal.

№	Chemical formula	Value, %
1	SiO_2	64,1
2	Fe_2O_3	0,21
3	Al_2O_3	32,72
4	CaO	< 0,1
5	MgO	0,28
6	SO_3	< 0,025
7	TiO_2	1,7
8	P_2O_5	0,12
9	Na_2O	< 0,2
10	K_2O	0,52

3.3 Results of balance experiments

Six balance experiments on low temperature pyrolysis of coal were carried out during the research and the results are presented in Table 4.

Table 4. Results of low-temperature pyrolysis process of coal.

№	Uploaded by	Received									
	Sample masses, г	Semi-coke		Dry resin		External water		Pyrogenetic water		Gas and losses	
		г	wt, %	г	wt, %	г	wt,%	г	wt, %	г	%
1	50,42	42,82	84,92	2,47	4,91	2,10	4,17	0,92	1,82	2,11	4,18
2	51,00	43,14	84,59	2,63	5,15	2,13	4,17	1,07	2,11	2,03	3,98
3	51,00	43,14	84,59	2,89	5,69	2,03	3,99	1,47	2,88	1,47	2,88
4	51,00	43,12	84,55	2,82	5,53	2,04	4,00	1,38	2,70	1,64	3,21
5	51,00	43,53	85,36	2,45	4,80	2,04	4,00	0,96	1,88	2,02	3,96
6	51,00	43,12	84,55	2,38	4,67	1,90	3,72	1,50	2,94	2,10	4,12
Average values		-	84,76	-	5,13	-	4,00	-	2,39	-	3,72
Convergence of results			0,25		0,33				0,45		0,45

The obtained results of low-temperature pyrolysis of coal showed that the main products of pyrolysis of the studied coal are semi-coke, tar and combustible gas, the average values of which (from 6 experiments) are 84,76%, 5,13% and 3,72%, respectively. At that, semi-coke is extracted in the greatest quantity. These results compare well with similar results obtained in [14] for 2 coal samples from Nariinsukhait and Tavantolgoi deposits at 500 °C. For these coal samples, the yields of semi-coke, tar and combustible gas were respectively: 93,0 %, 1,1%, 2,5% (for Nariinsukhait deposit) and 92,3%, 2,5%, 2,3% (for Tavantolgoi deposit). It should also be noted that the convergence of the ob tained results of 6 experiments is quite satisfactory.

3.4 Characterisation of pyrolysis products

The products of coal pyrolysis are gas, tar with bottom water and semicoke. In order to conduct a study of the composition of pyrolysis products it was necessary to accumulate about 50 grams of tar with bottom water and collect a sufficient amount of gas. Therefore, one experiment was performed on an enlarged retort with a 1 kg fuel loading to accumulate tar. However, all calculations and balances are presented based on the averaged results of 6 pyrolysis experiments.

3.4.1 Characteristics of pyrolysis gas

Pyrogas was sampled at 2 different temperatures: 480 °C and 520 °C, corresponding to the beginning of gas release and the period of maximum gas release for the most accurate calculation of its heat of combustion. Table 5 shows the results of analyses of the component composition of the obtained pyrolysis gas, % (vol.).

Table 5. Component composition of pyrolysis gas.

Temperature selections	CO_2	H_2S	H_2	N_2	CH_4	CO	C_2H_6	C_2H_4
480 °C	16,27	1,27	3,99	3,78	39,71	12,16	9,74	2,99
520 °C	8,16	1,27	8,64	1,54	50,19	13,77	9,50	1,82
Cf. value	12,21	1,27	6,33	2,66	44,96	12,97	9,63	2,41

In the obtained pyrolysis gas, CH_4 (44,96%), CO_2 (16,27%), CO (12,16%), C_2H_6 (9,74%) are present in the highest amounts in descending order. The remaining components make up less than 4% in the gas. Calorific value of gas was calculated according to the empirical formula of Mendeleev D.I. Calorific value of gas (lowest) according to averaged data was 7731,95 kcal/kg. This high-calorific gas was obtained mainly due to high concentrations of methane and ethane. The calculated density of the gas according to average data is 1,13 kg/m^3.

3.4.2 Characteristics of of total coal pyrolysis tar

The total tar is a dark viscous liquid, which is lighter than water, with a characteristic odour. The tar collected from different six experiments was separated from water. The tar was dehydrated to investigate the physico-chemical characteristics.

Physico-chemical parameters of the resin were: density (kg/m^3)−0.83; relative viscosity−2.17; kinematic viscosity (cSt)−13.22; flash point in an open crucible−75 °C; solidification temperature−7 °C. The component composition of coal tar is indicated in Table 6.

Table 6. Component composition of coal tar.

Component name	Content, %
Phenols	16,13
Pyridine bases	2,23
Carboxylic acids	0,32
Neutral hydrocarbons	33,92
Mechanical impurities	19,96
Carbenes, asphaltenes	20,30
Osmolators	7,10
Elemental composition:	
Carbon	80,68
Hydrogen	9,56
Sulphur	1,20

Nitrogen Oxygen	1,48 7,08
Heat of combustion, lowest, kcal/kg	8745,14

As can be seen from the results obtained, the main components of the obtained resin are neutral hydrocarbons (33.92%), carbenes and asphaltenes (20.30%), phenols (16.13%), and osmoles (7.10%). Pyridine bases and carboxylic acids are present in small amounts (less than 3%).

The dehydrated resin was subjected to distillation. The results of the distillation are presented in Table 7.

Table 7. Resin distillation results.

Distillation temperature interval, °C	Fraction yield %
n.a. = 69 69 - 180 180 - 280 280 - 337 > 337 k.k. = 337	- 6,60 24,40 21,50 46,37 1,13
Total	100

The fraction up to 180 °C can be evaluated as petrol, its yield is insignificant. Fractions related to diesel fuel (in the temperature range 180-230 °C) and boiler fuel (at temperatures > 280 °C) are more than 50%. The cube residue remains fluid at normal temperatures.

3.4.3 Characteristics of germinal water

The results of the study of sub-mill water composition are presented in Table 8.

Table 8. Characteristics of sub-mill water.

Name indicators	Univ. measurements	Values
pH	-	9,38
Chemical oxygen demand	mgO/l	60,0
Volatile with phenol vapour	g/l	0,9
Pyridine bases	g/l	2,4

Sulphates	mg/l	0,05
Chlorides	mg/l	0,003

3.4.4 Characteristics of semi-coke

Characteristics of semi-coke obtained as a result of coal pyrolysis are presented in Table 9.

Table 9. Characteristics of semi-coke from coal.

Name of indicator	Content on dry weight, %	Table of Contents organic mass
Mass fraction of ash (A)	35,00	-
Volatile substances (V)	10,81	16,63
Carbon	60,73	93,43
Hydrogen	2.74	4,21
Total sulphur	0,40	0,61
Oxygen	0,63	0,97
Nitrogen	0,50	0,78
Heat of combustion (lowest), kcal/kg	5587,19	

3.5 Thermal balance of coal pyrolysis

Calculation of the thermal balance was carried out on the average yields of products obtained during thermal decomposition of coal in the temperature range of 220-520 ° C. The yields of products calculated per dry mass of initial coal and their heat of combustion are presented in Table 10.

Table 10. Heat balance of coal pyrolysis.

№ n/a	Pyrolysis coal	Product yield, %		Combustion heat per working mass, $Q_н^p$, kcal/kg	Heat balance kcal/kg
		per analytical weight	on dry mass		
1	Initial coal	-	100	5752,81	5752,81
Coal pyrolysis products					

1	Semi-coke	84,76	88,29	5587,19	4735,70
2	Resin	5,13	5,34	8745,14	448,62
3	Pyrogenetic water	2,39	2,49	-	-
4	External water	4,0	-	-	-
5	Gas	3,72	3,87	7731,95	287,63
Total		100	100	-	5471,95
Imbalance					280,86 (4,88%)

As can be seen from Table 10, the heat balance mismatch is less than 5% (4.88%), which is quite acceptable and satisfies the requirements for the limits of acceptable random mismatch error.

4 Conclusion

The conducted study of the process of low-temperature pyrolysis of coal of "Saryadyr" deposit showed that the main products of pyrolysis are semi-coke (84,76%) and in small amounts−combustible gas (3,72%) and tar (5,13%). The semi-coke is a high-quality low-sulphur solid fuel. The obtained semi-coke is characterised by low volatile yield (10,81%) and high calorific value (Q = 5587,19 kcal/kg) and such product can be used as an effective smokeless fuel and as a reducing agent for metallurgical industry. The combustible gas obtained from coal also has high calorific value. Thus, valuable chemical products obtained from coal can be effectively utilised in the field of energy.

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