Investigation of oil shale pyrolysis process: physicochemical properties and decomposition products

Ayat Sabitov[1], *Gartzen* Lopez[2], *Togzhan* Mashan[1], *Lyazat* Kusepova[1]. *Yelaman* Aibuldinov[3] and *Eldar* Kopishev[1*]

[1]L.N. Gumilyov Eurasian National University, Faculty of Natural Sciences, Department of Chemistry, Astana, Kazakhstan
[2]University of the Basque Country, Bilbao, Spain
[3]L.N. Gumilyov Eurasian National University, Research Institute of New Chemical Technologies, Astana, Kazakhstan

Abstract. In the article pyrolysis of Kazakhstan oil shale with determination of physical and chemical properties of oil shale and products of its thermal decomposition is carried out. Elemental analysis of oil shale and analysis of mineral part of oil shale were carried out. Four parallel experiments of oil shale pyrolysis process were carried out, as a result of which the yields of such products as semi-coke, pyrolysis oil, combustible gas were determined, as well as their main characteristics (component composition, calorific value, etc.) were determined. The convergence of the results (from 4 experiments) is quite satisfactory.

1 Introduction

Oil shale is an important energy resource containing kerogen [1]. Dry distillation of oil shale can produce shale oil and gas, which can be further processed to produce various chemical products such as petrol, paraffin, diesel fuel and others. The Republic of Kazakhstan has huge oil shale reserves, which makes it an important strategic resource comparable to oil reserves [2,3]. The controlled pyrolysis process of oil shale produces better quality products. Temperature conditions play an important role: the optimum temperature range for pyrolysis is between 500 and 550 °C, which ensures a high yield of oil shale [3,4].

Studies also indicate the importance of the choice of heat transfer medium for oil shale pyrolysis[5,6]. For example, the use of water vapour in the convective heating of oil shale increases the efficiency and quality of the resulting products [7,8]. This is due to the chemical interaction of high-temperature water vapour with kerogen, which changes the oil and gas recovery characteristics [9,10].

Thus, research in the field of oil shale pyrolysis and its further processing plays an important role in the energy strategy of many countries, and the optimisation of oil shale extraction and processing processes is a key direction in the development of this industry [11,12].

* Corresponding author: kopishev_eye@enu.kz

The aim of this work is to study the pyrolysis process of oil shale from the "Kenderlyk" deposit (Kazakhstan) with the determination of physical and chemical properties of oil shale and products of its thermal decomposition [13].

2 Research methodology

To analyse the initial oil shale, an analytical sample was prepared. To evaluate the chemical composition of coal ash, a sample of 10 grams was prepared.

Crushed oil shale is mixed with crushed solid organic component, the temperature of the maximum decomposition rate of which differs from the temperature of the maximum decomposition rate of organic matter of HS by no more than 5°C [14,15]. They are pyrolysed at 520°C for 80 minutes according to the heating regime given in Table 1. The pyrolysis resin extracted from the vapour-gas mixture is distilled to obtain petrol, diesel fractions and distillation residue with boiling point above 350°C [16–18]. This residue is mixed with a liquid product of petroleum origin with a boiling point above 350°C containing emulsion stabiliser - asphaltenes and 2-6.5% of organic sulphur compounds per elemental sulphur. Aqueous solution of the catalyst precursor is emulsified in the obtained mixture, from which after mixing the emulsion with hydrogen and heating under hydroconversion conditions a dispersed sulfide hydroconversion catalyst is formed [19,20]. After hydroconversion, the liquid hydroconversion product is distilled. Gasoline fraction of hydroconversion is combined with gasoline fraction obtained during distillation of pyrolysis resin, and diesel fraction obtained during hydroconversion is combined with diesel fraction obtained during distillation of pyrolysis resin.

Table 1. Heating mode of oil shale suspension.

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

3 Results and their discussion

3.1 Characterisation of feedstock

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

Table 2. Characteristics of feedstock.

Components	Conditional designation	Indicators per weight, %		
		analytical	dry	combustible
Moisture	W	0,5		
Ash	A	52,24	52,50	
Sulphur	S	1,00	1,00	2,11
Carbon	C	22,79	22,90	48,21
Hydrogen	H	2,29	2,30	4,84
Nitrogen	N	0,50	0,50	1,05
Oxygen	O	20,70	20,80	43,79
Heat of combustion, lower	Ql	1929.7 kcal/kg		
Heat of combustion, highest	Qh	2030.4 kcal/kg		

The analysis of the mass fraction of chlorine and arsenic showed the following values: Cl - 0.058%, As - 0.0039%. The obtained indicators correspond to "traces" and are not further taken into account.

3.2 Characterisation of oil shale ash

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

Table 3. Chemical composition of the mineral part of oil shale.

№	Substance	Sample, %			
		OS-1	OS-2	OS-3	OS-4
1	SiO_2	57,2	54,3	60,3	58,8
2	Al_2O_3	11,2	10,8	9,4	9,7
3	Fe_2O_3	7,4	5,9	6,8	6,4
4	CaO	4,6	4,9	6,8	5,7
5	MgO	3,2	3,4	1,5	2,8
6	S	2,8	2,5	1,6	1,9

7	K_2O	1,3	2,2	1,6	1,4
8	TiO_2	2,6	3,5	2,9	2,4

3.3 Results of balance experiments

During the research 4 balance experiments on pyrolysis of oil shale were carried out, the results of which are presented in Table 4.

Table 4. Pyrolysis product yield.

№	Sample	Pyrogenetic moisture, Wd, %	Oil, %	Semi-coke, %	Gas and losses, %
I	OS-1	1,5	9,8	80,8	7,9
II	OS-2	1,7	8,6	81,5	8,2
III	OS-3	2,2	5,9	83,2	8,7
IV	OS-4	2,3	7,4	82,3	8,0

3.4 Characterisation of pyrolysis products

The products of coal pyrolysis are gas, oil and semicoke. In order to conduct a study of the composition of pyrolysis products it was necessary to accumulate about 50 grams of oil and collect a sufficient amount of gas. Therefore, one experiment was carried out on an enlarged retort with a 1kg fuel loading to accumulate tar. However, all calculations and balances are presented based on the averaged results of 4 pyrolysis experiments.

*3.4.1 Characteri*stics of pyrolysis gas

The pyrogas was sampled at the temperature: 500 °C, corresponding to the beginning of gas release. Table 5 shows the results of analyses of the component composition of the obtained pyrolysis gas, % (vol.).

Table 5. Component composition of pyrolysis gas.

Component, Parameter	Formula	Samples			
		OS-1	OS-2	OS-3	OS-4
Methane	CH_4	1,11	0,34	0,12	2,01
Ethane	C_2H_6	1,33	0,41	0,14	2,41
Propane	C_3H_8	1,38	0,43	0,15	2,51
Bhutan	C_4H_{10}	0,55	0,17	0,06	1,00

Pentane	C_5H_{12}	0,15	0,05	0,02	0,27
Ethylene	C_2H_4	1,52	0,47	0,16	2,75
Propylene	C_3H_6	1,65	0,51	0,18	2,99
Butylene	C_4H_8	1,11	0,35	0,12	2,01
Hydrogen	H_2	1,00	3,26	7,42	0,12
Carbon monoxide	CO	44,64	43,40	0,50	0,50
Nitrogen	N_2	1,10	1,30	2,40	1,20
Carbon dioxide	CO_2	41,48	46,44	86,93	80,32
Hydrogen sulphide	H_2S	2,98	2,87	1,81	1,91
Lower heat Qn	kJ/kg	12 706,85	7 992,83	1 608,22	12 676,69
Density	kg/m^3	1,58	1,56	1,79	1,90
Air for combustion	m^3/m^3	3,07	1,87	0,51	3,36

In the obtained pyrolysis gas, CO_2 (63,79%), CO (22,27%), H_2S (2,39%), C_3H_6 (1,33%) are present in the highest amounts in descending order. The remaining components make up less than 10% 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 8 746,15 kJ/kg. Low calorific value of gas is caused by high concentrations of carbon monoxide and carbon dioxide. The calculated density of gas according to the average data is 1.71 kg/m^3 .

3.4.2 Characteristics of pyrolysis oil

The oil is a dark viscous liquid, which is lighter than water, with a characteristic odour. The oil collected from four experiments was separated from water. Elemental analysis of oil are presented in Table 6.

Table 6. Elemental analysis of oil.

№	Sample	Oil						
		C, %	H, %	N, %	O, %	S, %	HHV, kj/kg	HHV, kcal/kg
I	OS-1	84,6	10,5	0,9	1,8	2,2	41921,9	10014,6
II	OS-2	85,3	9,8	0,6	2,3	2,0	41203,9	9843,1

III	OS-3	79,4	9,1	0,3	9,7	1,5	37463,9	8949,6
IV	OS-4	82,5	9,6	0,5	5,7	1,7	39600,4	9460,0

As can be seen from the results in obtained, the oil contains a high amount of carbon in it, with low sulphur content, which increases its calorific value, the results are presented in Table 7.

Table 7. Physico-chemical parameters of oil.

Sample		25°C - 200°C, %	200°C-360°C, %	>360°C, %	ρ, kg/m^3	flash point, °C
I	OS-1	4,6	26,7	68,7	896	308
II	OS-2	3,4	25,4	71,2	891	301
III	OS-3	2,1	20,1	77,8	909	327
IV	OS-4	2,9	22,5	74,6	903	315

Physico-chemical parameters of the oil were: density (kg/m3)−0.83; flash point in an open crucible−313 °C; pour point−6 °C.

3.4.3 Characteristics of semi-coke

Characteristics of semi-coke obtained as a result of coal pyrolysis are presented in Table 8.

Table 8. Elemental analysis of semi-coke.

№	Sample	Semi-coke						
		C, %	H, %	N, %	O, %	S, %	HHV, kj/kg	HHV, kcal/kg
I	OS-1	14,4	1,1	0,4	10,6	0,7	5192,1	1240,3
II	OS-2	15,6	0,8	0,3	9,6	0,5	5302,3	1266,7
III	OS-3	8,9	0,5	0,2	5,5	0,2	3069,4	733,2
IV	OS-4	10,9	0,6	0,2	6,2	0,4	3817,8	912,0

4 Conclusion

The conducted research of low-temperature pyrolysis process of oil shale of "Kenderlyk" deposit has shown that the main pyrolysis products are semi-coke (81,95%), combustible gas (8,2%) and pyrolysis oil (7,9%). Semi-coke is a high-quality low-sulphur solid fuel. The obtained oil is characterised by low volatile yield and high calorific value (Q = 9567,18

kcal/kg) and such product can be used as an effective smokeless fuel and as a reducing agent for metallurgical industry. The product obtained from oil shale does not have a high calorific value. Thus, valuable chemical products obtained from oil shale can be effectively used in the field of energy.

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