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RADIATION-THERMAL DESULPHURIZATION OF ORGANIC FUELS

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Abstract: The regularities of desulphurization of bituminous lignite, oil-bitumen and oil-bituminous rocks under simultaneous impact of gamma-radiation and heat were studied. The absorbed dose in organic fuels changed within the limits of 7, 5-30,0 kGy. The rate of gas formation, decreasing of initial mass of irradiated samples and the content of sulfur in the initial fuels has been defined as a basic index of process. The gaseous products H_2, CH_4, H_2S and COS were identified. The selectivity and specific energy consumption are discussed in the radiation-chemical desulphurisation of organic mass of fuels under simultaneous impact of gamma-radiation and heat.

Keywords: bituminous lignite, oil-bitumen, oil-bituminous rocks, γ-radiation**,** desulphurization, gases

1. Introduction

The most harmful effect on environment of lignite and oil-residues that used as fuel and chemical raw material is due to its sulfur content. The processes such as combustion, gasification, hydrogenation and coking of coal lead to the transformation of sulfur to the SO_2, H_2S, CS_2, COS gases and other harmful substances and are causing environmental pollution. The sulfur content of organic fuels on average is between 0,2 and becomes as high as 10% for high sulphuric coals. At the same time organic fuels may be considered as a rich source of an important raw material such as sulphur. Desulfurization processes used for prevention of environmental pollution and production of sulfur is one of the important processes in organic fuel technology. Desulfurization of organic fuel has been investigated by mechanical, electrostatic, magnetical, biological and chemical methods [1-3]. It is reported that 85-90% of pyritic sulfur in coals could be removed by these methods. It was shown that 85% of total sulfur and 25% of organic sulfur could be removed by a chemical method conducted in oxygen and steam medium under the temperatures of 400-600^{o}C. It was also stated by several researches that 60% of total sulfur could be removed by radiation effects [4].

The study of radiation-chemical transformation of coal has great importance for creation of scientific basis of radiation-chemical technology of fossil fuels, establishment of the role of radiation in genesis and metamorphism of fossil fuels as well as determination of radiation stability of carbonaceous materials used in nuclear technology.

Researches on radiation-chemical processes of transformation of fossil fuels have been spent for last 30 years in USA, Japan, Italy, Russia, Azerbaijan and other countries within the framework of the Programs on atomic-hydrogen Energy and new methods of processing of fossil fuels [4-7]. Radiation-stimulated processes in oil-residues (tar, fuel-oil, heavy fraction of oil refining products, etc), bituminous rocks and bituminous lignites are not regularly investigated.

In this work the regularities of desulfurization of organic fuels under gamma-radiation and heat were studied.

2. Methods and objects

In the experiments the samples of oil-bituminous rock from Kirmaku (Azerbaijan) deposits, oil bitumen and bituminous lignite from Silopi deposit samples of Turkey were used. The content and some characteristics of samples are indicated below:

Oil-bituminous rock (OBR) from deposit Kirmaku (mass %): oil content in the rock- 8.2-9.4 , humidity – 3.14, clay- 25.7, sulphur- 0.8 ; ratio in organic mass H/C= 0.14, bulk weight - 1.5 g/cm3.

Oil-bitumen: Element content (mass %): - C-84,67, H-10.5, S- 2.0, O- 0.5, N-0.6; flash point- 170-180^{o}C, density-0.905 g/sm^{3}, funnel viscosity- 6.2 cSт at 20^{o}C.

Bituminous Lignite from Silopi deposit of Turkey (mass % on dry mass): ash-26.3, sulphur-4.75, humidity- 5.7; calorific value 4384 kCal/kg.

Experiments were performed under simultaneous impact of gamma-radiation and temperature in the thermostable static conditions. In the experiments, the dose rate of gamma-radiation (P) was 2.1 Gy/s, temperature (T) was 400^{o}C and absorbed dose (D) was 7.5-30 kGy. The selection of 400^{o}C temperature is associated with activation of thermal diffusion processes and breaking reactions in the organic fuels.

Total sulphur content of coal was determined before and after the test by laboratory device MET and gas products were analyzed by gas chromatography. The decreasing of amount of organic material and ash ration were determined by gravimetrically.

In the experiments five parameters were investigated to characterize the radiation-thermal desulfurization processes:

1. Degree of desulfurization (K) expressed as

$$K = \frac{S_0 - S}{S_0} * 100\%$$

So, S -initial and final concentration of sulfur in the samples.

2. Degree of breaking organic mass (μ) expressed as

$$\mu = \frac{M0 - M}{M0}.100\%$$

M_0, M -initial and final amounts of organic mass of samples.

3. Selectivity of process α is expressed as $\alpha = \frac{K}{\mu}$

4. Specific energy consumption (ε) for desulfurization process expressed as

$$\varepsilon = \frac{\delta E}{\delta S}$$

δS – Decrease of sulphur in organic fuels

δE- Energy spend to desulphurization

Sulphuric gas formation and sulphur in gaseous products

3. Results and discussion

In the determination of optimum conditions for organic fuels desulfurization, the conditions for which K and α parameters are maximum, ε and μ parameters are minimum were investigated.

Parameter must be maximum in optimum conditions by experimental and kinetic calculations optimum amount of radiation energy was determined.

The results of kinetics (t = 60-240 min, or 7.5-30,0 kGy) of desulphurization processes for all 3 samples at 400^{o}C temperatures are shown in figures 1-3.

As seen from the figures 1-3 the rate of decomposition of organic matter is 2.2-3.8 times smaller than desulphurization rates. At the biggest radiation doses (30 kGy) the coefficient of

selectivity are 3.8 times for oil-bitumen, 2.9 times for lignite and 3.5 times for OBR. This coefficient depend each from absorbed doses and type of organic fuels and increases by absorbed doses for all types of fuels.

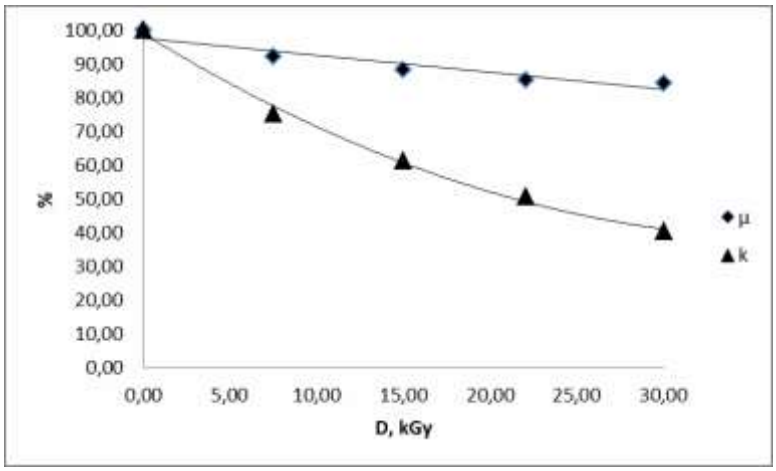

Fig. 1. Dependence of organic mass decomposition and desulphurization of oil-bitumen on absorbed dose at the radiation –thermal process.

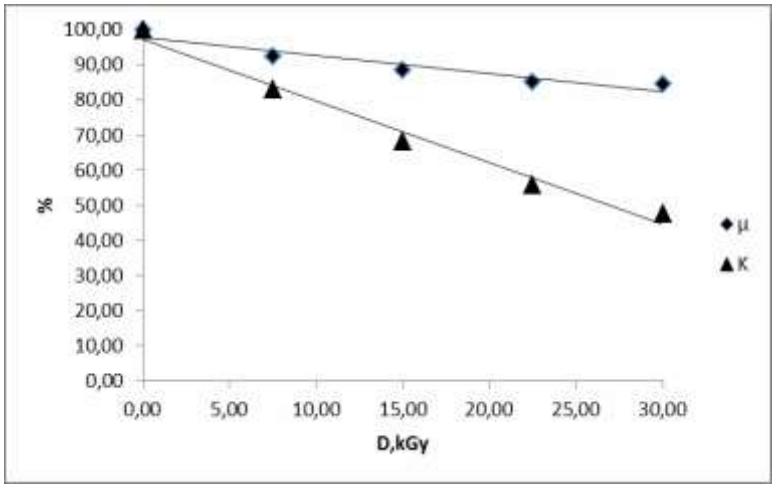

Fig. 2. Dependence of organic mass decomposition and desulphurization of Silopi bituminous lignite on absorbed dose at the radiation –thermal process.

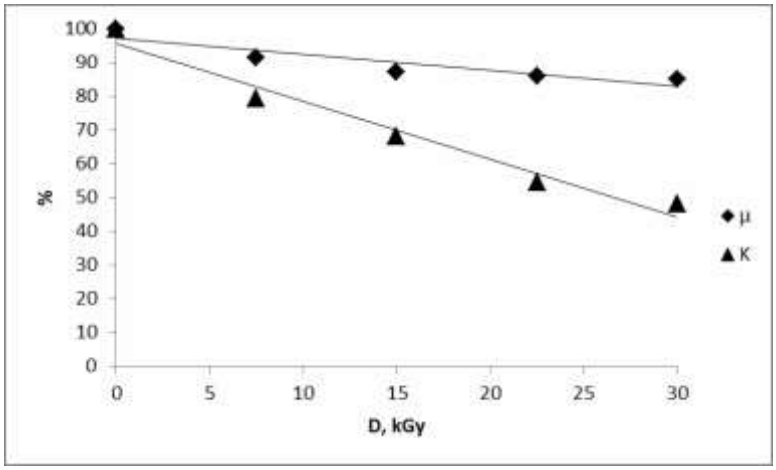

Fig. 3. Dependence of organic mass decomposition and desulphurization of oil-bituminous rock on absorbed dose at the radiation –thermal process.

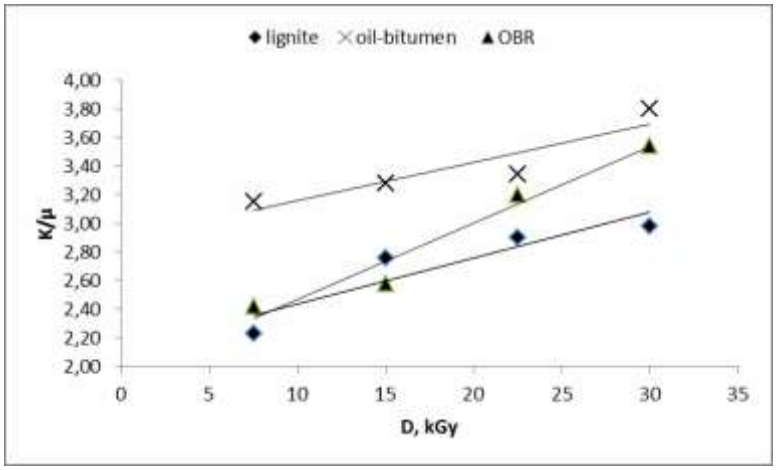

Fig. 4. Dependence of selectivity (k/μ) of desulphurization process on irradiation dose at the radiation-thermal processing of oil-bitumen, bituminous lignite and oil-bituminous rock.

Dependence of selectivity on type of fuels is connected with differences of initial concentration of sulphur in the fuel and their composition/ structural particulars.

Specific radiation energy consumption for desulphurization processes were determined in all conditions for each 3 samples and adduced in the table 1.

Table 1. Dependence of Specific radiation energy (ε, kWh/kg S) consumption for desulphurization processes on absorbed dose

Dose, kGy	Oil-bitumen	OBR	Bituminous lignite
7,5	0,42	1,27	0,25
15,0	0,52	1,64	0,27
22,5	0,63	1,71	0,29
30,0	0,71	2,01	0,33

As seen from the table 1 the increasing of ε by desulphurization degree associated with location of sulphuric contained chemical bonds in the organic mass of fuels. First of all sulphur in the peripheral and bridge bonds are separated, the more energy requires the separation of sulphuric bond in the aromatics units, on this reason ε increases.

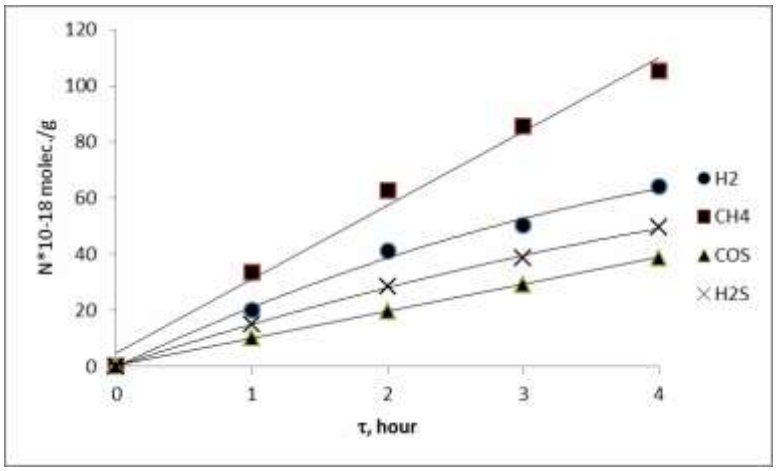

Fig. 5. Kinetics of gas formation ($N*10^{-18}$ molec./g) at the radiation-thermal processing of oil–bitumen; P=3.5 Gy/s, T=400°C.

Gas formation kinetics, including sulphur containing gases COS and H_2S indicated (fig.5) that even up to 30 kGy absorbed dose only 10% of sulphur emissioned as a COS and H_2S. Probably, about 90% of sulphur is separated in forms of merkaptans and other volatile this organic compounds in conditions.

4. Conclusion

The mechanisms of selective desulphurization of coals by the radiation-thermal method are given below

- There are 16 electrons in sulphur atom, on the other hand hydrogen and carbon atoms in organic structure of fuels contains less electrons. For this reason radiations had a great effect in breaking of chemical bonds of sulphuric compounds.
- Due to π electrons the fuels containing organic mass with aromatic part is resistive to radiation effect and absorbed energy is directed to aliphatic and bridge groups. Consequently, under the action of gamma radiation, it well be easier to separatet sulphur from aliphatic and bridge bonds and other nonaromatic parts.

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РАДИАЦИОННО-ТЕРМИЧЕСКОГО ОБЕССЕРИВАНИЯ ОРГАНИЧЕСКИХ ТОПЛИВ

И.И. Мустафаев, Х.М. Махмудов

Резюме: Изучены закономерности десульфурации битуминозного лигнита, нефтеного лигнита, нефтебитумных пород при одновременном воздействии гамма-излучения и тепла. Поглощенная доза в органическом топливе изменилась в пределах 7,5-30,0 кГр. В качестве основных показателей происходящих процессов были определены скорости формирования газа, снижение

исходной скорости серы и органического топлива. Были определены газы H_2, CH_4, H_2S и COS. Обсуждается селективность и удельный расход энергии радиационно-химических процессов обессеривания.

Ключевые слова: битуминозный лигнит, нефтяной битум, нефтебитумные породы, γ-излучение, обессеривание, газы.

ÜZVÜ YANACAQLARIN RADİASİYA-TERMİKİ KÜKÜRDSÜZLƏŞDİRİLMƏSİ

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Xülasə: Qamma-şüalanma və istiliyin birgə təsiri altında neft bitumunun, bitumlu liqnitin və neft-bitum süxurunun kükürdsüzləşdirilməsi proseslərinin qanunauyğunluqları tədqiq olunmuşdur. Üzvü yanacaqda udulan doza 7,5-30,0 kQr intervalında dəyişmişdir. Baş verən proseslərin əsas göstəriciləri kimi qaz yaranma prosesinin sürəti, üzvü yanacağın kütləsinin və kükürdün azalma sürətləri təyin edilmişdir. H_2, CH_4, H_2S və COS qazları təyin edilmişdir. Radiasiya-kimyəvi kükürdsüzləşdirmə prosesslərinin selektivliyi və məxsusi enerji sərfi müzakirə olunur.

Açar sözlər: bitumlu liqnit, neft-bitumu, neft-bitumlu süxur, γ-radiasiya, kükürsüzləşdirmə, qazlar