EFFECT OF PRELIMINARY IRRADIATION OF KARAMAN-ERMENEK LIGNITE ON THEIR THERMAL DECOMPOSITION

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ABSTRACT

Influence of γ–irradiation of lignite from Karaman-Ermenek deposit of Turkey on its following thermal decomposition was studied. The absorbed dose of preliminary irradiation is D = 5.4-410.4 kGy, the lignite decomposition temperature is t = 350-600°C. H_2, CO, CO_2 and hydrocarbon gases C_1-C_4 are identified as a products during lignite semi coking. It's shown that the quantity of semi coke gas volume and hydrocarbon gases concentration extremely depend on the preliminary radiation dose, the maximum gas volume corresponds to the absorbed dose 20-70 kGy. This experimental fact is explained by the competition between radiation induces processes of destruction and polycondensation in the lignite organic mass.

1. INTRODUCTION

The possibilities of application of ionizing radiations for the stimulation of gasification, pyrolysis, semi coking, extraction and desulphurization of fossil fuels and adsorbent production from coke are shown in the works[1-7]. Destruction and polycondensation processes behavior in the lignite organic mass of Soma deposit of Turkey under the influence of ionizing radiations is demonstrated by the application of ESR, IRS, differential-thermal analysis methods[8] e.t.c.

It's shown that the limits of an absorbed dose providing these processes behavior are changed depending on the solid fuel metamorphism. The preliminary lignite γ-irradiation influence of Karaman-Ermenek deposit of Turkey on gas generation process during subsequent semi coking is investigated in this work that presents an interest for explanation of the mechanism of ionizing radiations effect on fossil fuels. The characteristics of Karaman-Ermenek washed lignite are: % Humidity-15.6 %, Ash- 19, 26 %, % Sulfur-2.01%, Calorific value-3775 kcal/kg

2. EXPERIMENTAL

The study of preliminary lignite irradiation influence on its further semi coking was carried out on the sequential experiments of lignite irradiation and irradiated samples semi coking. The milled lignite samples with the sizes below 3 mm were dried under vacuum at 105°C temperature during an hour. Under such conditions water and occluded gases are wholly released from the lignite, but chemical processes still don't take place. The samples were irradiated in an ampoule from a molybdenum glass and vacuum-treated till residual pressure P=10 Pa. The lignite samples irradiation was carried out at 35-40°C on "MPX- γ-30" gamma- radiation source Co-60. The absorbed dose values of preliminary irradiation D1=5.4, D_2=19.2, D_3=65.6, D_4=169.6, D_5=410.4 kGy are selected. The dose rate is 0.76 Gy/s.

After irradiation the ampoules were open and approximately 1gramm of the sample was put into a quartz reactor on facility for the study of semi coking regularities of the irradiated lignite samples. The control experiments on unirradiated lignite samples were also made for the purpose of identification of preliminary lignite irradiation role on gas generation process during its further semi coking.

An experimental facility scheme for the study of the semi coking products formation regularities at the thermal decomposition of lignite is shown on fig.1.

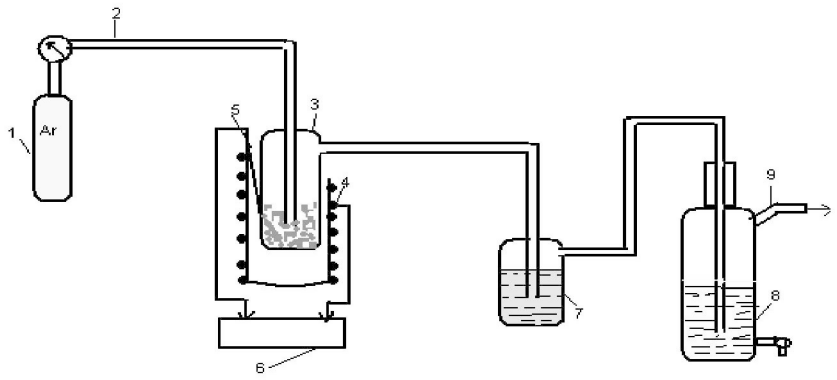


Fig. 1. The scheme of Laboratory setup for study of gas formation regularities at the semi coking of irradiated lignite samples. 1-Argon gas tube , 2-communication pipe, 3-reaction vessel, 4-heating system, 5- thermocouples, 6-Thermoregulation-measuring instrument, 7- Receiver for liquid products, 8-gas meter, 9- exit to chromatography.

The temperature in the quartz reactor (3) was maintained by means of thermostating system (6) consisting a heating system (4), thermocouples (5), measuring instruments. The temperature rise speed in the reactor is 10-12 degree/s, the maximal semi coking temperature is 600°C. The liquid products are condensed in a receiver (7) for the liquid products, the gas products are gathered in a gas-volume (8). An exit to gas chromatography is joined to a communication pipe (9). An argon (1) was passed with 3 ml/s speed till 200°C heating temperature through the reactor-communication pipes (2) and the detector for oxygen role exception during reactor heating in the thermal process. The resulting gas volume was measured by means of graded gas meter indication, the gas products content was determined on the gas chromatography apparatus "LXM-8MD".

3. RESULTS

The dependence of total volume of the lignite semi coking products on the preliminary lignite irradiation dose is shown on fig.2.

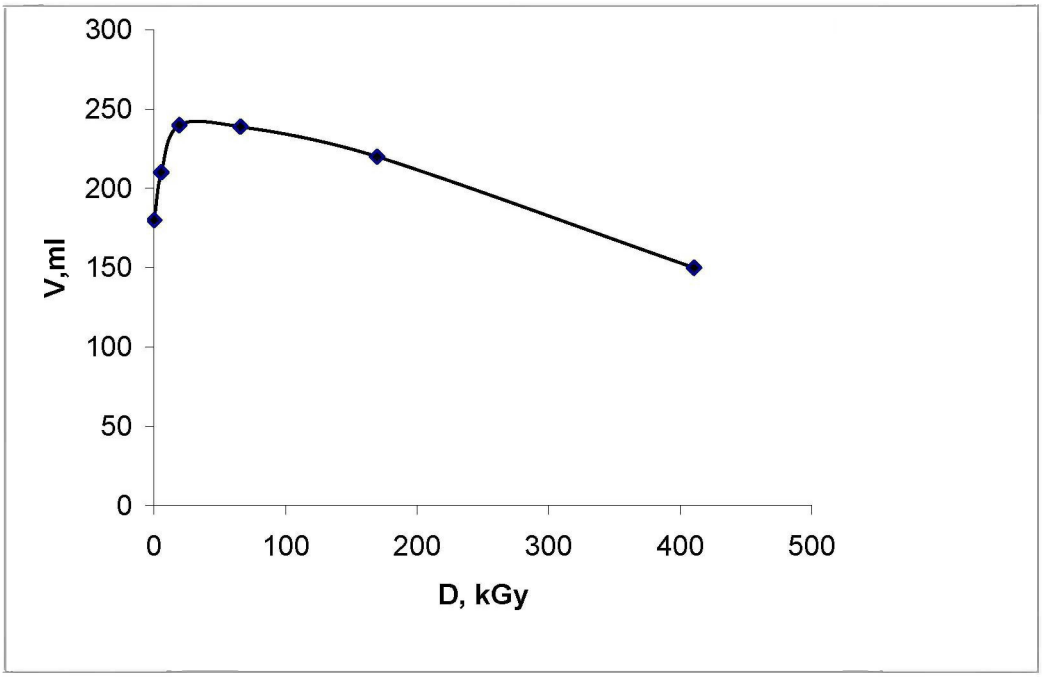


Fig. 2. Influence of adsorbed dose of preliminary irradiation on semi coking gas volume

It's evident that the preliminary irradiation dose within 0-410,4 kGy extremely influences on the gas volume formation during the lignite semi coking till 600ºC. If in the unirradiated sample gas volume is 180 ml, then the gas volume grows and reaches 240 ml at D=19,2 kGy during its irradiation by dose 5.4 and 19.2 kGy. Further increase of the absorbed dose by lignite causes reduce of the semi coke gas volume. At the absorbed dose 410.4 kGy gas volume becomes 150 ml that is 20% lower than in virgin lignite sample.

In the semi coking gas composition content of H_2, CO, CH_4 isn't changed essentially (see table 1), deviation from average value doesn't exceed 10-15%. The content of CO_2 with respect to virgin lignite reduces to 30%.

Table 1. Influence of adsorbed dose of preliminary irradiation on semi coking gas content (vol.%)

D,kGy	0	5.4	19.2	65.6	169.6	410.4
H_2	15.1	15.2	16.1	16.7	16.3	17.1
CO	23.1	23.2	24.2	24.3	22.4	23.1
CH_4	19.0	21.2	21.1	22.8	22.3	22.4
CO_2	28.5	25.6	20.5	18.3	20.2	22.5
C_2-C_4	7.5	11.7	14.5	15.1	13.1	6.4
Non-identified	6.8	3.1	3.6	2.8	5.7	8.5

The most interesting results are achieved for the hydrocarbon gases C_2-C_4. The dependence of total content of the hydrocarbon gases C_2-C_4 on the preliminary irradiation absorbed dose is of synchronous character with change of the semi coking gas total volume dependence to the adsorbed dose (see fig. 3).

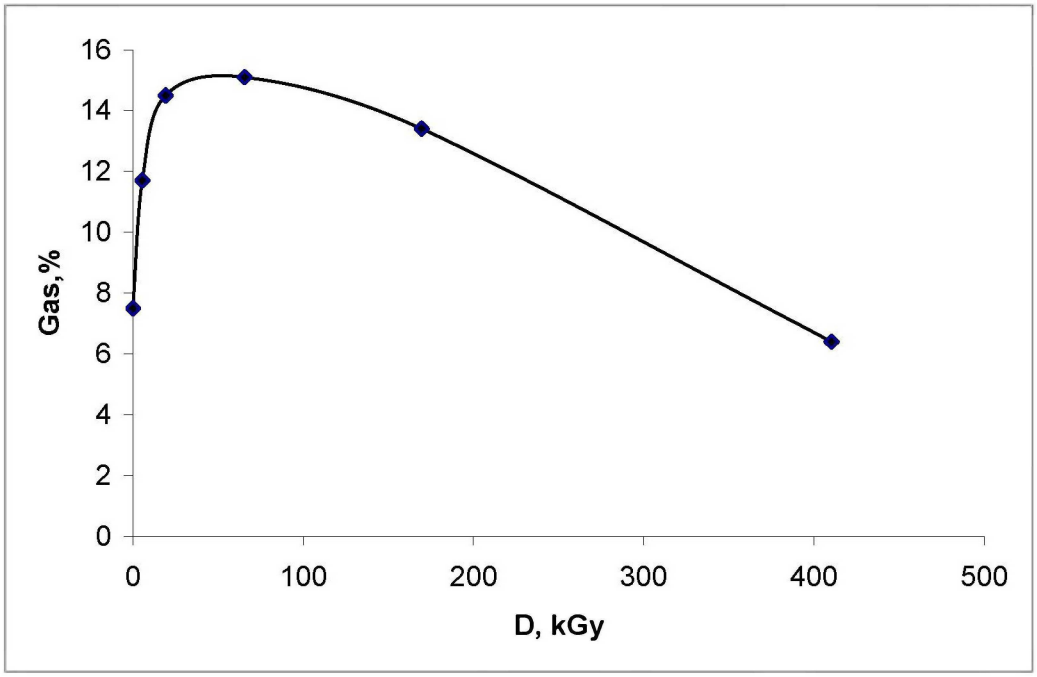


Fig.3. Influence of adsorbed dose of preliminary irradiation on total content of hydrocarbon gases C_2-C_4 in the semi coking gas

The influence of temperature on the semi coke gas volume in virgin sample and at the absorbed dose two values corresponding to minimum (410.4 kGy) and maximum (19.2 kGy) gas yield is studied. The results are shown on fig. 4. As shown in figure about 89% of all gas is released till temperature 450ºC in the sample irradiated by the dose 19.2 kGy. At the same time in all 62% and 46% of semi coking gas are released in virgin sample and the irradiated lignite by the dose 410,4 kGy at such temperature, accordingly.

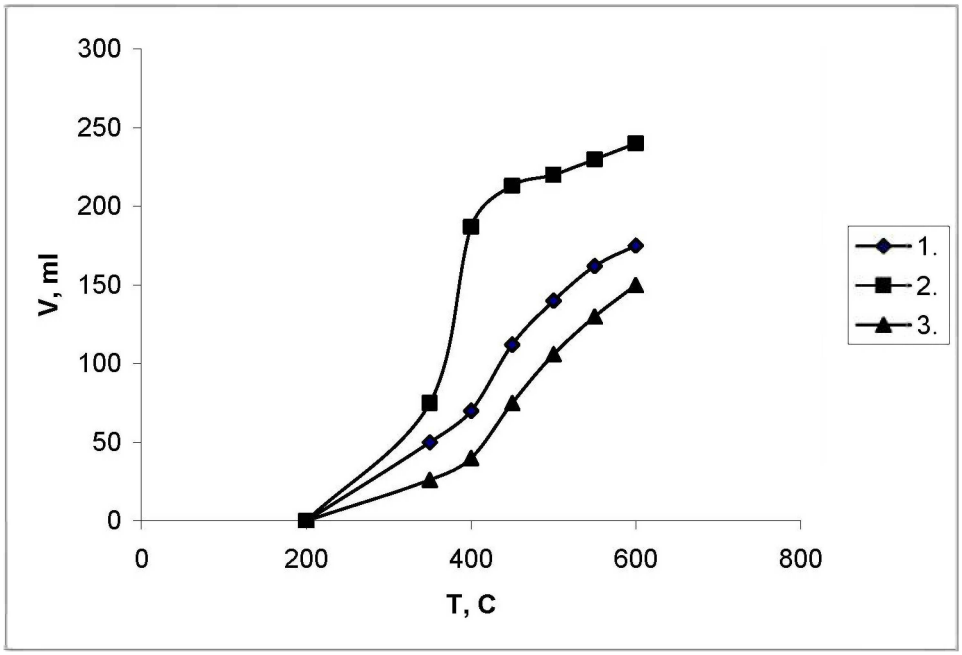


Fig. 4. Influence of temperature on semi coking gas volume: 1- virgin sample, D=0, 2- D=19.2 kGy, 3- D= 410,4 kGy

This shows that the preliminary lignite irradiation causes not only increase of the semi coking gas volume, but also the shift of maximal gas release to low-temperature region at lower doses (D < 100 kGy) of preliminary irradiation. In the virgin (curve 1) and the irradiated at D =410.4 kGy (curve 2) samples gas formation according to temperature grows till 550°C monotonically, further tendency of saturation is observed.

4. DISCUSSION

Thus the obtained experimental results unambiguously show that the process of stable defects accumulation able to exist at room temperature takes place during the preliminary lignite irradiation. One should not draw an unambiguous conclusion about nature of these defects on the basis of this data. Earlier we showed that the reduce of paramagnetic centers connected with poly-conjugated bonds breakage takes place during irradiation [9]. The breakage in poly- conjugated lignite organic mass was shown also by means of infrared spectroscopy. In all evidence the extreme dependence of the gas outlet on the preliminary irradiation dose is connected with the competition of destruction and polycondensation radiation-induced processes. In our case the dose till 100 kGy stimulates destruction during the heating; during its further increase polycondensation following by the cross linking of the high-molecular-weight poly-conjugated structure of the organic mass of lignite is observed. The concentration of these active centers generated during the lignite irradiation may be estimated. According to the conception of multimeric structure of organic mass of lignite the conventional molecular mass of an organic part is approximately 2000. There are $6 \times 10^{23}/2000=3\ 10^{20}$ associates in 1g of lignite.

At the absorbed dose 100 kGy the concentration of generated by gamma radiation active centers in the coal is

$Na=GaI\ 10^{-2}t = GaD\ 10^{-2}$

where t- irradiation time, I- dose rate

Substituting in Ga=7 bond/100 eV and D=100 kGy ($6\ 10^{20}$ eV/g).

Then Na equals Na=7 x $6\ 10^{20}$ eV/g x 10^{-2} bond/ eV = $4.2\ 10^{19}$ bond/g

Thus per 1g. lignite may be formed $4.2\ 10^{19}$ broken bonds at dose 100 kGy during irradiation.

Thus approximately 14% of the multimeric links will be activated at the doses 100 kGy. At the highest doses the concentration of these bonds will be so great, that they can react with each other via cross-links. The increase of coal thermal stability during its irradiation by the dose more than 100 kGy witnesses about polycondensation processing in the lignite organic mass under the irradiation influence. In this case split bonds at the doses D= 100 kGy are joined crosscut and form cross-linked structure in the organic mass of

lignite. The associates of the coal organic mass earlier joint with each other by electron-donor-acceptor bonds are joined by valence bonds during the irradiation by the doses higher than 100 kGy. This attaches to lignite organic mass the properties of high thermal stability and so the reduce of gas generation speed and the depletion of the hydrocarbons product are observed during the semi coking.

5. CONCLUSION

Destruction and polycondensation processes take place during the preliminary γ-radiation of organic mass of lignite depending on an absorbed dose. The dose limits for predominant reactions of one of these processes are in the range of 100-150 kGy for washed lignite Karaman-Ermenek deposit of Turkey.

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