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EPR Study of Coal under Heat Treatment

S. Munkhtsetseg* , G. Erdene-Ochir, R. Galbadrakh, L. Enkhtur, O. Oyunkhand[1]
[1]Department of Physics, School of Arts and Sciences, Natural Science Division, National University of Mongolia, Zaluuchuudiin Urgun Chuluu Str.1, Ulaanbaatar 210646, Mongolia, *e-mail: munkhtsetseg_s@num.edu.mn

Abstract
The high temperature has been set up directly in the ampoule contained coal sample in the resonator. It has been experimentally established that a thermal reaction allows detecting transient, short lived, highly reactive radicals in the coal structure.

Low carbon content, brown coals such as Tevsh, Tugrug and Khotgor have showed similar behavior under the heat treatment. However, it is complicated for the high carbon content coals in the range of the used temperature. The complexity structure of coal is independent of the microwave power and the used temperature range.
Keywords: coal, EPR spectroscopy, heat treatment.

Изучение термообработанных углей по ЭПР спектроскопии

С. Мунхцэцэг , Г. Эрдэнэ-Очир, Р. Галбадрах, Л. Энхтөр, О. Оюунханд
[1] - Монгольский государственный университет, 210646, Монголия, г. Улан-Батор, ул. Залуучуудын өргөн чөлөө 1.
е-майл: munkhtsetseg_s@num.edu.mn

Аннотация
Установлена высокая температура прямо в ампуле содержаемой образец угля размещающем в резонаторе. Эксперментальные данные показывают что при термообработки углей позволяет обнаружить коротко живущих, высоко-реагирующих радикалов в структуре углей по ЭПР спектроскопии.

Бурые, мало содержащих углеродов угли как Тэвш, Төгрөг и Хотгор являются одними с схожими характерами при термообработке. Зато угли высокосодержащих углеродов как Сайхан-Овоо реагируются неоднородно, имеющим комплексными структурами. Обнаруженные комплексные структуры не зависят от микроволновых напряжений или от температуры.
Ключевые слова: уголь, ЭПР спектроскопия, термо обработка

I. INTRODUCTION

Coals come to be distributed in various parts of Mongolia with over 152 billion tons of coal reserves, mainly lignite, brown and bituminous metamorphism [1]. So far, the country coal use has been mainly for the nation's electricity generation, precisely, the electricity and heating supply is directly from coal burning in electrostations and homes over the years and this will stay as the largest single source of overall domestic energy production in the nearest future.

This has been called the investigation on Mongolian coal structure and chemical processing [2-16] and it will increase with a growing demand of an interest on coal mining.

Furthermore, for the proper use of national wealth such as a coal which can be converted through proven, existing modern technology into clean coal it is highly required to push the structural analysis of Mongolian coals in an advanced level.

For the characterization of coal, the coal rank studies, the type of organic (e.g. macerals) and inorganic (e.g. minerals, trace elements) constituents within coal play significant role. In addition, for energy production applications the essential properties such as calorific value, volatile matter, moisture content, elementals (carbon, hydrogen, oxygen, sulphur, nitrogen) content and behavioral characteristics as a liquefaction yields', coking propensity and combustion efficiency are in basic interest.

In the latter case the paramagnetic centers naturally present in coal can serve as probes to study local properties without affecting the original composition of coal.

In the present work a high temperature electron paramagnetic resonance (EPR) spectroscopy is applied to study coals and their reaction. The heat treatment on coal samples inside the EPR cavity has the capability of monitoring thermally induced transient free radicals in coals.

II. EXPERIMENTAL

Samples. Six coal samples from the different Mongolian coal deposits were studied by EPR spectroscopy.

Sample mass is measured on the Mettler Toledo AE 260 micro balance and size on SMZ-140 series Stereomicroscope with magnification range 40.

Sample preparation for the analysis was performed in accordance with standard procedures of coal chemistry: the samples were mixed, crushed initially in a breaker and then in a mill to a size of 0.05 mm or less for elemental analysis measurement and to a size of up to 5 mm for spectroscopic analysis.

Further the coals in this work were grouped into their provenance by basins or areas in the country which can be the followings: Western Mongolian province (Mongol Altai, Valley of Great Lakes), Southern Khangai, Ikh Bogd, and Ongi river basins (Valley of Lakes), South Gobi basin (Southern Mongolia), Orkhon-Selenge area (Central and Northern Mongolia) and Eastern Mongolian province (Eastern Mongolia) how determined in [5].

Grouped coal places and their deposit names and as well as the element contents are given in the table 1. The determination of the elements C, H, N, O and S is carried out with instruments of the company LECO at the Micro Laboratory for Organic Chemistry (ETH, Zurich). The samples were digested first and the combustion products as carbon (CO_2), hydrogen (H_2O), sulfur (SO_2) and oxygen (CO_2) are analyzed quantitatively by infrared spectroscopy.

Nitrogen (N_2) is determined by a thermal conductivity detector. These variables are measured in weight percent (wt. %) and are calculated in the air-dried (ad) base.

TABLE I: Elemental analysis of coals

Basin/Area sample	**Coal deposit/ Abbreviation**	**C^{ad}, wt.%**	**H^{ad}, wt.%**	**O^{ad}, wt.%**	**N^{ad}, wt.%**	**S^{ad}, wt.%**
Eastern Mongolian province	Tevsh (Te) Tugrug (Tu)	51.13 59.41	5.47 3.28	35.40 3.92	0.77 1.45	0.36 0.34
Southern Khangai, Ikh Bogd, and Ongi river basins	Khotgor (Kho)	68.20	4.56	11.08	2.03	0.40
Western Mongolian province	Maanit (Ma) Khushuut (Khu)	74.75 80.85	5.56 4.09	9.14 5.79	1.65 2.07	0.47 0.33
Central and Northern Mongolia	Saikhan-Ovoo (SO)	84.26	2.84	5.94	2.21	0.35

EPR measurement. Measurements were performed with a Bruker Elexsys II E500 spectrometer (ETH, Zurich) equipped with a high-temperature EPR cavity.

Experiments are conducted at a frequency 9.20 GHz and modulation of 100 kHz provided by the modulation unit. A microwave power of 30 dB is used throughout the measurements.

The spectrometer was equipped with a super high Q-factor resonator (ER 4122 SHQE) which has a cylindrical shape TE011 cavity.

For a standard procedure, 20 mg samples a size of ~ 0:05 mm or less placed in 0.4 mm quarts EPR sample tube, which was inserted directly into the high-temperature cavity.

Modulation amplitude and time constant of EPR registration were chosen from well-known requirements for undistorted registration of the first derivative resonance absorption signal by magnetic induction.

EPR spectra of the studied coals were registered as the first derivative of the microwave absorption versus applied magnetic field. The parameters of the EPR spectra: g-factor, linewidth (ΔH_{pp}) and integral intensity (I_{pp}) were evaluated.

g-factor was determined as $g = h\upsilon / \beta H_r$, where h is the Planck constant, g the Bohr magneton, υ the microwave frequency, and H_r is the resonance magnetic induction. The linewidth (ΔH_{pp}) was determined as the difference of field positions of maximum and minimum of the first derivative EPR spectrum. The integral intensity (I_{pp}) is the distance between maximum and minimum of the first derivative EPR spectrum. Heating available temperature range was from room temperature (~ 26^0C) to 500^0C.

To prevent oxidation by air, the sample tube was degassed at low vacuum (a few Pascal's) and owed by nitrogen gas (kept at a constant flow rate).

In this experiment, the only relevant ESR-parameter is the peak-to-peak amplitude of the first derivative signal in arbitrary units, taken as a measure of the number of radicals in the sample.

The EPR spectrum was measured at every 500C and during heating and cooling (after heat treatment) room temperatures as well. EPR microwave power saturation was measured at every 100^0C heating temperatures.

EPR spectra of the coals were first measured at room temperature and after the samples were cooled EPR spectra also were measured at room temperature.

Simulation of EPR spectra was done using the Matlab package EasySpin [17].

III. EPR MEASUREMENT RESULT AND DISCUSSION

Changes in the EPR parameters, such as peak-to-peak amplitude (I_{pp}), linewidth (ΔH) and g-factor, at room temperature before heating and cooling of the studied coals can be seen in the table 2.

The EPR spectra of coals registered at room temperature before heat treatment and cooling are shown in figure 1.

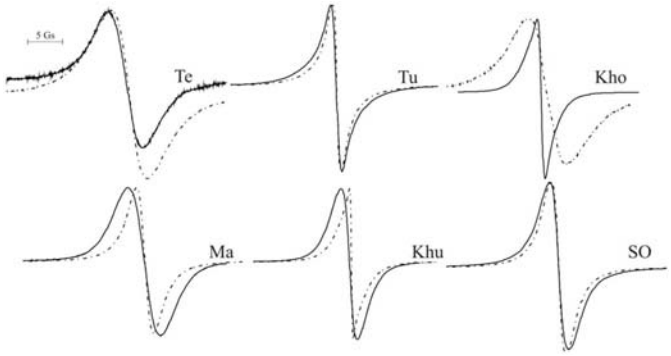

FIG. 1: Normalized EPR spectra of coals (solid line spectrum - before heating and dashed line spectrum - cooling/after heating. Abbreviations of coal sample names are quoted from table 1.

TABLE II: EPR parameters at room temperature (1 - heating and 2 - cooling)

Coal sample	EPR parameters						
	I_{pp}/I_{ppmax}		$I_{pp}(1)=I_{pp}(2)$	ΔH_{pp}, Gs		g-factor	
	1	2		1	2	1	2
Tevsh	0.005	0.018	0.277	6.45	6.84	2.0075	2.0073
Tugrug	0.098	0.219	0.447	1.61	1.20	2.0028	2.0028
Khotgor	1	0.012	83.33	2.10	11.24	2.0013	2.0029
Maanit	0.001	0.072	0.014	7.09	3.86	2.0074	2.0073
Khushuut	0.051	1	0.051	4.49	0.93	2.0035	2.0035
Saikhan-Ovoo	0.007	0.693	0.010	1.61	2.08	2.0045	2.0031

Figure 2 shows the general profile of peak-to-peak amplitude as a function of temperature for the studied coals.

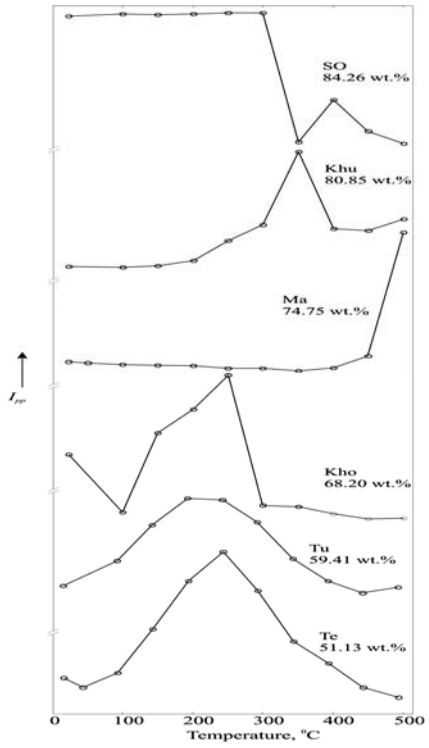

FIG. 2: Temperature dependence on peak-to-peak amplitude of EPR spectra of coals

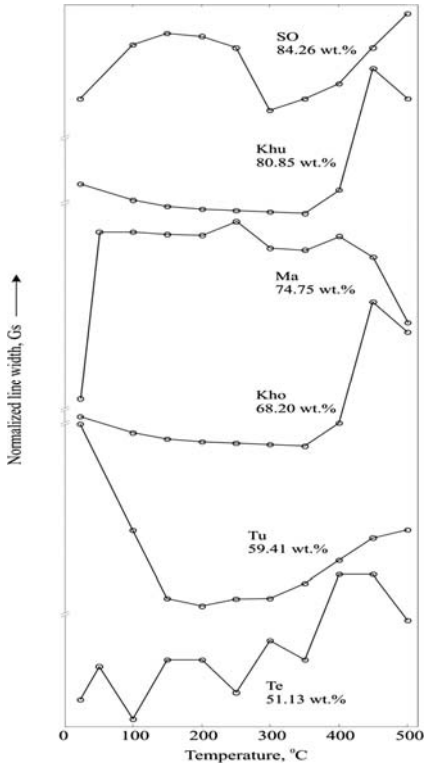

FIG. 3: Temperature dependence of normalized EPR spectra line width of coals

The dependence between the temperature and the peak-to-peak amplitude corresponds to the Curie law for the high carbon contained coals Maanit, Khushuut and Saikhan-Ovoo (Table 2, cooling from 500^0C to room temperature) but contradictious for the lignite coals such as Tugrug, Tevsh and Khotgor.

These dependences behave similarly with maximum around 20^0 - 300^0C for the lignites Tevsh and Tugrug and sub-bituminous Khotgor coal. This increase can be correlated with the weak bonds such as benzyl phenyl ether type C-O linkages or dibenzyl type C-C bonds dissociation in coal structure [18, 19]. Further, a decrease of the amplitude till 500^0C causing the major loss of hydrogen is observed. This bond breakup point could not been reached in the used temperature interval for the bituminous coals (Saikhan-Ovoo, Khushuut and Maanit).

Temperature dependence for these coals behaves differently. Its peak-to-peak amplitude is high from room temperature up to 300^0C and goes abruptly down at high temperatures for Saikhan-Ovoo coal. Saturation curve presents the disappearance of the narrow line from this temperature. This phenomenon can be observed in Maanit coal at 500^0C where it has maximum point of amplitude and appearance of the narrow EPR line. The observed changes in linewidth were relatively small in Tevsh, Tugrug, and Saikhan-Ovoo. The linewidth has strongly broadened in Khotgor coal.

Generally, linewidth dependence versus temperature plots the jumps from 26 to 100^0C (fig 3). Despite the tendency of line width broadening for Tevsh and Tugrug and decreasing for Khotgor and Khushuut coals in the up going temperature can be considered.

g-factor decreases in the increasing temperature for the coals. In Khotgor coal g-factor increases large from 400 to 500^0C.

The saturation measurement of these coals at every 100^0C temperatures behaved differently for each coal. In the figures 4 below show the power saturations for each coal.

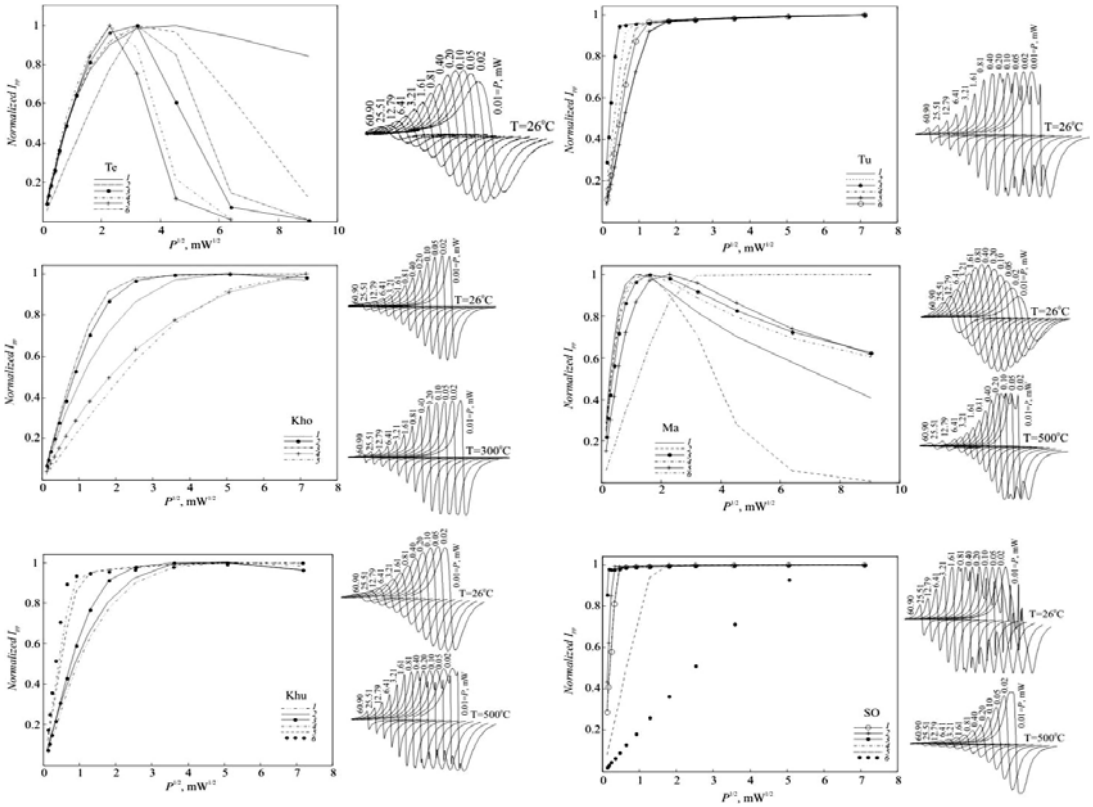

FIG. 4: Power saturation curves for studied coals at different temperatures (1 - room temperature (~26^0C), 2 - 100^0C; 3 - 200^0C; 4 - 300^0C; 5 - 400^0C; 6 - 500^0C)

For Tevsh coal the EPR is singlet and all dependences from room temperature to 500^0C are homogeneous and saturated, presenting the maximum at the lower power level, following a considerable EPR intensity quench (fig 4 Te: dependences 1-6).

EPR spectrum of Tugrug coal consists of two components (broad and narrow) at high power level. The saturation at all temperatures is exhibiting leveling that no having subsequent decrease in EPR signal amplitude (fig 4 Tu: dependences 1-6).

At lower temperatures (from 26 to 200^{0}C) EPR spectrum homogeneously saturated with maximum at high power (~ 25 mW) on Khotgor coal (fig 4 Kho: dependences 1-3). At 300^{0}C this singlet spectrum slightly broadens at high power. From 400^{0}C the homogeneous saturation degree is getting smaller that can be caused the appearance of the spins with short relaxation time (fig 4 Kho: dependences 4-6). From room temperature up to 400^{0}C the homogeneous saturation with exhibition of maximum at low power level were observed for Maanit coal (fig 4 Ma: dependence 1-5), but at 500^{0}C the EPR spectrum was split to two components and the saturation curve leveled at high level of powers (fig 4 Ma: dependence 6).

Homogeneous, single spectrum at room temperature of the Khushuut coal starts to split to two parts from temperature 100^{0}C. EPR spectra consist of two components show the similar behavior of saturation that it saturated at lower power and keeps the EPR signal intensity (fig 4 Khu: dependence 1-6). At higher microwave power levels at temperature interval of 26 - 400^{0}C EPR spectrum of the Saikhan-Ovoo coal is a two-component and the spectrum saturated at low power levels (fig 4 SO: dependence 1-5). At 500^{0}C the spectrum saturated at highest power level showing splitting on it.

IV. CONCLUSION

In the conclusion, one can consider that the established thermal reaction allow to detect transient, short lived, highly reactive radicals. Brown (lignite) coals show the similar behavior in the heat treatment. However, it is complicated for the high rank coals in the used temperature.

The paramagnetic centers related to the singlet EPR spectrum of brown (lignite) Tevsh coal is the most homogeneous type among the studied coals.

The complexity structure of coal is independently of the coal rank, the microwave power and the used temperatures. The "natural" asymmetry of the EPR line of Khotgor coal can be not due to the complex structure of the organic matter.

The paramagnetic centers with low concentration and short relaxation time were formed at high temperatures (400 and 500^{0}C).

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