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FTIR Study of Enriched Bituminous Ukhaa-Khudag Coal

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Abstract

In the present work we pay an attention to the molecular structural changes between raw coal and its enriched, dense productions. Bituminous Ukhaa-Khudag coal in the form of an enriched, dense coal product is currently used as an energy source by Mongolian consumers for everyday need.

There are three types of samples from one source: it is a raw coal (sample 1) and two of industrial products as an enriched, dopant (organic based) added coal (sample 2) and simply enriched coal (sample 3). The raw coal general characterization is given through the elemental analysis, thermogravimetry analysis, moreover functional groups were identified by Fourier Transform infrared spectroscopy. The differences in the FTIR spectra of the samples were done.

Some details are as follows: hydroxyl group vibrations are existing, rather weak in agreement of TG result; vibrations of aliphatic group were rarely in the long wave near region, carbonate minerals in the region of 1300-900 cm^{-1} are visible but overlapped, and an isolated out-of-plane deformational vibration (around 800 cm^{-1}) or two-adjacent (800-750 cm^{-1}) or three-adjacent (around 700 cm^{-1}) of sp^2-hybrid bonded aromatic CH_x-groups were still presenting.

After the processing hydroxyl group bands were affected in enriched coals, sample 2 and 3. In the spectrum of the sample 2 the long wave bands were intensively blurred.

Industry processing retains an amount of water in the productions. Water excess influenced absorbance bands were able to be removed via the drying processing, however, the affection to the spectral structure in sample 2 was unrecoverable.

Introduction

Few years ago, the Mongolian Government constitutionally forbade a use of direct burning of raw coal in the country, particularly in the capital city Ulaanbaatar, where a population density exceeds over one million, to decrease facing problem related to the air pollution and public health damage. Raw coal use was substituted by enriched, dense coal products. Several industries throughout the country produce these types of products. As industry raw materials in common, the bituminous coals are used therefore, technically the coal deposits around the city Ulaanbaatar can not be potential suppliers to them.

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By the geographical map of coal-bearing basins and deposits [1], the Ukhaa-Khudag deposit is located in the South Gobi basin in southern Mongolia. The deposit is currently under mining as an open-pit. Despite its remote location 600 km south of Mongolia's capital Ulaanbaatar Ukhaa-Khudag coal was chosen to be processed throughout the industries for its good general chemical and physical properties such as elemental content, coal rank, porosity index etc. The mineable reserves of the Ukhaa-Khudag coal is estimated approximately 300 million tonnes.

Enriching processing of the coal is as following: the raw coal was first water washed and released from the water by the gas pressure in the factory. It is an intermediate production. Thus the intermediate product was ground up to size of 0.5 to 0.7 mm and even less. During grinding certain physical indices (eg, coal moisture content) was controlled to optimize further processing. A dopant, a typical and commercially relevant organic based product, was added. The dopant was chosen as an indicator for changes in the coal structure to minimize coal smoke during the burning. Unnecessary substances, such as heavy elements were separated from this intermediate product and dopant mixture via placing it in a magnetic field, afterwards an enriched product (it is a clean mixture) was compressed into a shape and supplied into the public market.

Such enriched production has been in use of direct burning for years in the capital city Ulaanbaatar, Mongolia.

Currently there is no substitutional variant of this production, except raw coal, moreover enriched coal manufacturing increases by several hundred thousand tonnes annually for the domestic demand.

However, scientific evidences in quality and quantification of these enriched coal are rare in publishings. Recently used method of using corn starch to suppress coal dust in coal production [2] or to prepare high performance of porous carbon [3] showed promising results of quality improvement.

Fourier Transform infrared spectroscopy is widely used to structurally reveal coal characterization [4, 5, 6], since it can provide crucial information on the molecular structure of organic and inorganic components of coal. The present paper is about earning some information of the structural differences between raw coal and enriched ones (intermediate and final productions) to show qualitatively the coal structural improvement.

Experimental

Coal. The Ukhaa-Khudag raw coal was taken from the one borehole of the basin and labelled as "sample 1". Enriched, dopant added and compressed coal sample, labelled "sample 2" and enriched, power energy coal sample, labelled "sample 3" are from the factory located near Ulaanbaatar.

The sample preparation for the analysis was according to the standard procedures of the coal chemistry: A piece of coal was crushed initially and then milled to a size of $0.05\ mm$ or less in an agate mortar in an argon gas flow glove box. At last, the milled sample was kept in a Schlenk flask under argon gas.

Dopant. As a dopant, soluble corn starch ($C_6H_{10}O_5$), an organic polymer, a polysaccharide comprising of glucose monomers joined in α 1.4 linkages was chosen. The dopant sample is a finely dispersed, homogeneous powder.

Elemental analysis. Quantification of the elements C, H, N, O and S in the raw coal sample were done with instruments of LECO at the Micro Laboratory for Organic Chemistry (ETH, Zurich). After processing the combustion products - carbon (CO_2), hydrogen (H_2O), sulfur (SO_2) and oxygen (CO_2) were analyzed quantitatively by infrared spectroscopy. Nitrogen (N_2) was determined by a thermal conductivity detector. These variables are measured in weight percent (wt. %) and calculated in the air-dried (ad) base (see table 1).

Thermogravimetry analysis (TGA) was done on a Mettler Toledo TGA/SDTA851 thermobalance. The thermogravimetry scan was carried out from 30 to 1000^0C temperature interval in a flow of nitrogen gas of high purity nitrogen (20 ml min^{-1}). Fixed carbon (determined in the presence of air at 900^0C) and ash content (the residual weight loss) are not measured in this method for some technical reasons.

Table 1: Elemental analysis result of Ukhaa-Khudag raw coal from LECO

Element content, wt.%				
$C,^{ad}$	$H,^{ad}$	$O,^{ad}$	$N,^{ad}$	$S,^{ad}$
81.77	5.26	4.76	2.71	0.31

Inintially, the sample mass was 4.47 mg as measured on the Mettler Toledo AE 260 micro balance. Then, the sample was placed into the open alumni pan (70uL).

TG measurement is started with a cooled furnace and a cleaned pan. The pan is cleaned in a programmable furnace (Fisher Scientific) at 550^0C for 60 min. The total time of being in a furnace is approximately 18 min for one sample.

Determination of moisture content. Moisture held within the coal itself is known as inherent moisture and is analyzed. Moisture may occur in four possible forms within coal: surface, hydroscopic, decomposition and mineral moisture. The sample is heated up to $100 - 250^0C$ at a rate of 50^0C min^{-1} and is maintained to be at every 100^0C for 1 min. The weight loss is due to the water.

Determination of the volatile matter. Volatile components in coal are a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulfur. The sample is further heated up to 1000^0C at 50^0C min^{-1}and is maintained at every 100^0C for 1 min. The weight loss is due to volatile matter and total weight loss is due to coal volatile components.

The result from the TG method is a temperature-weight curve. The typical resulting curve is shown on figure 1. Two stages of weight are shown in figure 1 where a component loss is indicated. A calculation of the total weight loss values obtained from TG experiment are shown in table 2. The TG results in the table refer to a sample ground up to < 0.05 mm, the standard size for the proximate analysis. Two stages of pyrolysis of coal are found in two main temperature regions. The first with a small weight loss before 350^0C is to moisture elimination [7], it is somehow overlapped with a higher weight loss in the temperature range of $350 - 640^0C$, due to devolatilisation which results mainly from the decomposition of the organic coal substances and the mineral matter (water of hydration, carbon dioxide and sulphur compounds of the latter) [8]. Devolatilisation extends up to 850^0C and here corresponds to a secondary degasification or active decomposition in the result of an evolution of various hydrocarbon gases [9].

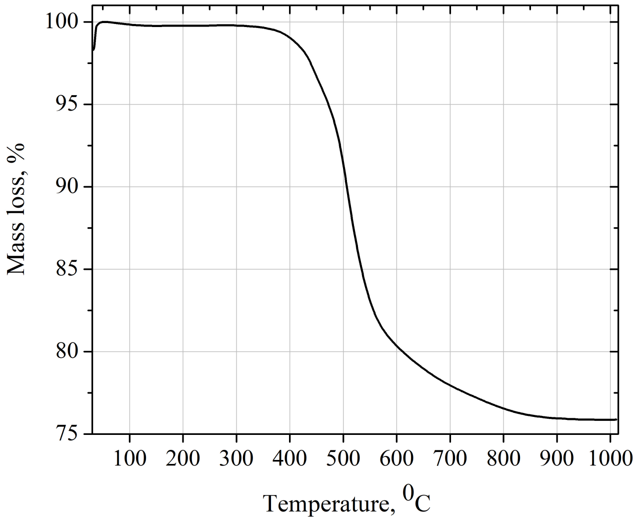


Fig. 1: TG curve for the Ukhaa-Khudag coal at a heating rate of 50^0C min^{-1} in the nitrogen atmosphere.

Table 2: Proximate analysis results of the studied coal Ukhaa-Khudag, its production and the material that used for the coal enrichment

Sample	TG parameters, wt.%		
	Moisture content	Volatile matter	Ash
Ukhaa-Khudag	0.23	24.12	0.34
Enriched, dopant added coal product$^{\oplus}$	6.38	18.59	23.59
Dopant* (Cornstarch, $C_6H_{10}O_5$)	13.0	-	0.30

Note: $^{\oplus}$the results are taken from the State inspector assessment numbered 02-04-407\286 authorized by City Inspection Service

*the results are taken from the product supplied organization

Experimental setup for spectroscopy. The functional groups of the prepared samples were detected by the In situ *Fourier Transform Infrared (FTIR)* Nicolet iS5 FTIR Spectrometer at the Laser II laboratory, NUM, in absorption mode. Samples were well ground using a mortar for the infrared measurement. Thus, every sample was scanned in the range from 400 to 4000 cm^{-1}. The beam splitter was Ge.

Experimental Results and Discussion

Analytical data is provided by FTIR spectroscopy measurement. Absorption bands are spread in the short-wave (3800 – 2800 cm^{-1}) and long-wave (1800 – 400 cm^{-1}) ranges of the FTIR spectrum (see. fig 2). In table 3 the characteristic organic absorptions and their assignments to the original coal are shown. In the spectrum of the raw coal, ”sample 1”, rarely visible weak peaks around 3684 and 3617 cm^{-1} are altered by nonbonded hydroxyl group, $O-H$ stretch, like phenols and alcohol [10]. The absorption at 3617 cm^{-1} is associated to a vibration in a hydrogen-bonded dimer in alcohol like

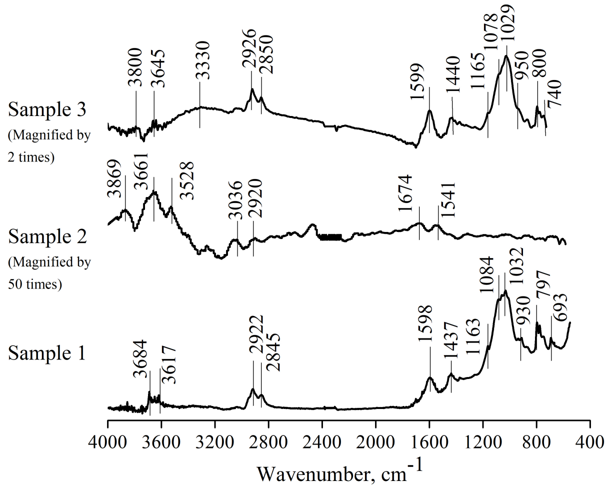
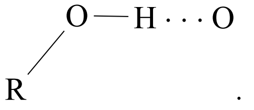


Fig. 2: The FTIR spectra of the samples. Ukhaa-Khudag raw coal labelled as ”sample 1”, enriched, dopant added and compressed coal sample, labelled ”sample 2” and enriched, power energy coal sample, labelled ”sample 3”. The spectra of the samples 2 and 3 are magnified by 50 and 2 times, corresponding their weak intensity compared to the raw coal spectrum.



Hydroxyl groups vibrations are intensively significant weak in sample 2.

In the region of the CH_x- group stretching vibration (3100 – 2800 cm^{-1}) there are observed two

Table 3: Absorptions in the coal samples (Sample 1 - raw coal of Ukhaa-Khudag, Sample 2 - enriched, dopant added and compressed Ukhaa-Khudag coal, Sample 3 - enriched, power energy Ukhaa-Khudag coal) under the current study (sh - shoulder peak)

Bands, cm^{-1}			Assignment
Sample 1	Sample 2	Sample 3	
	3869	3800	
3684, 3617 sh	3661, 3528	3645	aliphatic $O-H$ stretching
3000, 2960 sh,	3036, 2913	2926, 2850	aliphatic $C-H$ stretching
1598	1674	1599	aromatic ring stretch,high conjugated hydrogen bonded $C=O$
1437	1541	1440	bending of CH_2 and CH_3 groups
1163	-	1165	alkyl, ketones, group $=C-O$ stretching
1084, 1032	-	1078, 1029	mineral oxide stretch ($Si-O$ or $Al-O$)
930	-	950	isolated aromatic $C-H$,
797, 693	-	800, 740	2 or 3 neighbouring $C-H$ bending

intense absorption bands with maximum at 2922 and 2845 cm^{-1}. Bands at 2922 and 2845 are from the stretching (symmetrical and asymmetrical) vibrations of aliphatic group CH_2 and CH_3 relatively. Since a concentration of hydrocarbon is proportional to the integral intensity of the stretching band of CH_x- group [11], in these coals predominantly in a state of CH_2 is appropriate.

A broad band in the region of $1600-900$ cm^{-1} gives important information about the functional groups in the coal structure. Because of the overlap in this frequency range, interpretations are always ambiguous.

A peak centered near 1598 cm^{-1} indicates a carbonyl group in an aromatic ring characterized by sp^2-carbon or carbonyl absorption from conjugated hydrogen bonded carbonyl groups, or due to a donor and an acceptor interaction between aromatic carbon macromolecules.

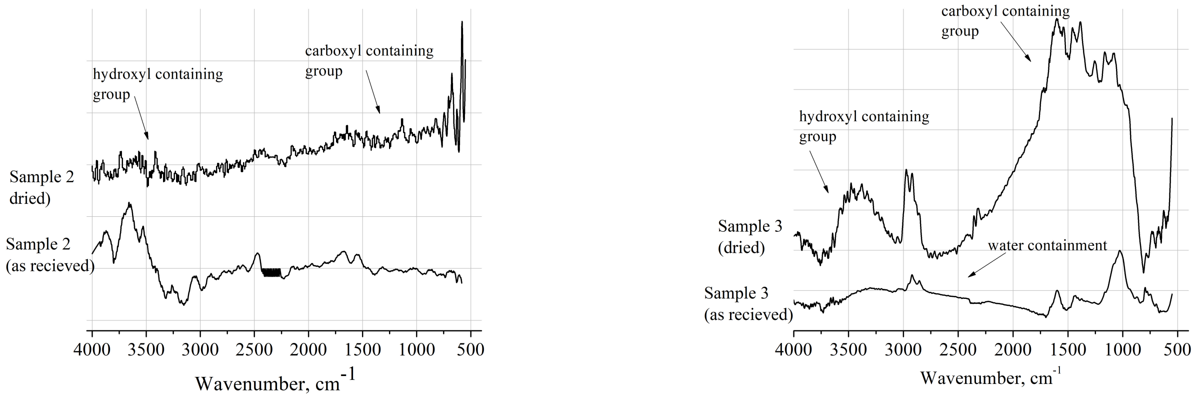
The band around 1437 cm^{-1} is assigned to the bending of CH_2 and CH_3 groups [12, 13]. The intensity of this band correlates preferentially with an intensity of bands from carbonate minerals in the region of $1300-900$ cm^{-1}. Despite the peak at 1437 cm^{-1} that contributes to the presence of minerals [10], the identification of minerals such as clay in the current broad region remains very difficult because of their complicated and non-constant composition and also because band positions can vary highly due to isomorphous replacements.

Bands in the wide interval of 1160-1000 cm^{-1} indicate mineral components in raw coal. The presence of the bands of 1163, 1084 and 1032 is followed a vibration near 750 cm^{-1} that is resulting from the quartz existency [10].

The prominent bands in the short-wave zone are three bands at 930, 797 and 693 cm^{-1} from an isolated out-of-plane deformational vibration (around 800 cm^{-1}) or two-adjacent (800-750 cm^{-1}) or three-adjacent (around 700 cm^{-1}) of sp^2- hybrid bonded aromatic CH_x-groups.

Generally, the mineral fraction of the coal is a poly-component system provided that one mineral is not predominant and a complexity of the overlapping may preclude a straightforward interpretation. Thus, in according to the literature [14, 15] the various spectral bands at 1032, 797 and 693 cm^{-1} and lower are compatible with the vibration of minerals in different types.

Regarding the spectrum of ”sample 2”, the enriched, dopant added coal is firstly, a low intense and contains very few vibration bands. Vibrations in the short wave zone (that is 1400-400 cm^{-1} in wave number) were obscured. Vibrations from carbonyl and carboxyl groups at 1674 and 1541 cm^{-1} are barely observed. These frequencies tend to red shift compared to the corresponding peaks in the raw coal spectrum. Bands around 3600 cm^{-1} are broader and blue shifted and relate to 3528 and 3661 cm^{-1} that means the processing of the enrichment is followed a weak interaction hydrogen bonds among



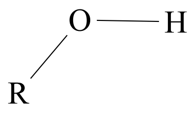
(a) (b)

Fig. 3: FTIR spectra a) sample 2, as received and dried b) sample 3, as received and dried. Samples were dried at 100^0C for 24 hrs for the removal of water content.

phenolic and carboxyl groups. Water is difficult to be totally removed, therefore, a vibration around 3869 cm^{-1} is in place. Mineral vibration bands were well eliminated by the washing and, magnetic cleaning process of the raw coal. The removal of various minerals is enhanced by adding a dopant to the coal (sample 2).

For the enriched, power energy coal ”sample 3”, a background broad band in the area of 4000 to 2000 cm^{-1} is clearly observed. TG data shows an extremely low moisture content (fig.1 and table 2) in the raw coal that is in good agreement with the corresponding frequency bands on the infrared spectrum. This suggests the containment of water in the sample 3 is higher than its raw coal. Relatively, a weak vibration around 3800 cm^{-1} and a broad band at 3330 cm^{-1} are observed in sample 3.

Quantitatively the same number of the vibration bands in the long wave region as in its raw coal has recorded in sample 3. It might be that a broad background band overlapped on the vibrations in the short wave area in sample 2 and 3 after the coal enriching processing is blurring the actual absorbance vibrations in this area. In other hand, this is the evidence of water containment due to the sample preparation regime in which the imperfection of water removal processing. The moist condition in coal processing allows bonds to form solutes. Water contains both hydrogen donor groups interacting with (halogenated compounds) and non-bonded electron pairs such as ethers, aldehydes and tertiary amines. The position of the band (around 3800 cm^{-1}) shows a vibration of $O-H$ stretching like



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Another broad band in this area at 3330 cm^{-1} in the sample 3 can be associated to normal ”polymeric” OH stretching. These hydroxyl compounds frequencies are stemming from the processing of the coal. Base on above, we removed excess water containment via drying sample 2 and 3 in an oven at 100^0C for 24 hrs in the presence of air and measured FTIR spectra (fig.3). In both samples water excess background spectra clearly removed as shown in figures 3a and 3b. In details, several absorption bands of OH stretching vibrations such as OH groups (3600 cm^{-1}), polymeric OH (ethers) (3300 cm^{-1}) were extracted in samples. Therefore, we see the actual functional groups existed in the samples. The absorption at 3400 cm^{-1} in dried samples (particularly, in dried sample 3) is evident of stability of self associated OH and $OH-\pi$ hydrogen bonds. Dried sample 2 still preserves absorptions around 3400 cm^{-1}, moreover, the carboxyl (in the 1700-1600 cm^{-1}) and mineral fragments in the long wave number (1000 - 400 cm^{-1}) now possibly are observable.

Conclusion

Structural characterization of enriched coal products, prepared from the well carbonized Ukhaa-Khudag coal, was made in the field of infrared spectroscopy. Carbon content in the raw coal was estimated by elemental analysis as high as 81.77 wt.%. In this analysis the content of hydrogen, oxygen, nitrogen and sulphur was determined as well. TG analysis reveals low content of moisture (0.23 wt.%) and volatile matter (24.12 wt. %) in the raw coal.

The registered vibration bands in the infrared spectrum of the raw coal were well related to the elemental and TG analysis results.

Enriched and dopant added ”sample 2” exhibits an essential change in the infrared spectrum, the main vibrations from the ”sample 1” tend to blurring. The coal enriching processing has resulted the blurring of hydroxyl and neighbouring aliphatic bands in the short wave and oxygen contained carboxyl and neighbouring aliphatic vibration in the long wave region. In sample 2 we see long wave vibrations after the drying process that demonstrates structural affections by doping processing.

The infrared spectrum of the ”sample 3” contains most of the peaks as in ”sample 1”. The processing induced broad band near 3330 cm^{-1} that is assigned to the normal ”polymeric” OH stretching. Moreover, hydroxyl group peak around 3800 cm^{-1} in the spectra of ”sample 2 and 3” is caused by the water existence during the coal enriching processing. Imperfection of industry processing leaves a certain content of water in the structure of the coal that gives a change in, particularly, spectrum integral intensity to decrease. Water excess removal shows the stability of self associated OH and $OH - \pi$ hydrogen bonds in the samples.

The results present a significance to the diminishing heavy volatile parts in the form of smoke or dust under the direct burning use of coal via removing functional groups in the structure.

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