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Investigation on Characterization and Pyrolysis of Some Coals from Mongolia

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ABSTRACT

This study reports the technical characteristics, the organic elemental composition of coal, and the inorganic elemental composition of coal ashes from four selected coals including Tavan tolgoi, Nariin sukhait, Baganuur and Shivee-Ovoo deposits in Mongolia. The thermal stability analyses of the organic mass in coal samples were also conducted with thermogravimetric analysis and discussed with the detailed mechanisms of the thermal decomposition of the coal organic mass. Furthermore, the coal samples were processed by pyrolysis at different heating temperatures and determined the yields of pyrolysis products such as hard residue, condensed liquid (tar and pyrolysis water), and uncondensed gas products. The coal ashes from the selected coals were also studied in detail and report that the ashes of high-rank coals of Tavan tolgoi and Nariin sukhait deposits have acidic character and ashes of low-rank coals of Baganuur and Shivee-Ovoo deposits have alkaline character. In addition, the coals samples from Tavan tolgoi, Nariin sukhait, Shivee-Ovoo, and Baganuur deposits were processed by pyrolysis at different heating temperatures and determined with the yields of pyrolysis products such as hard residue, condensed liquid (tar and pyrolysis water), and uncondensed gas products. The yields of hard residue from high-rank coals of Tavan tolgoi and Nariin sukhait were higher than that of low-rank coals of Baganuur and Shivee-Ovoo coal. The dewatered tar products of pyrolysis were investigated for chemical composition analysis.

Keywords: *High-rank coal, Low-rank coal, Bituminous coal, Thermogravimetric analysis, Thermal stability indices, Pyrolysis tar, Pyrolysis hard residue*

1. INTRODUCTION

Mongolia is among the 10 coal-rich countries in the world with 175 billion tonnes of geologically estimated coal resources including high-quality bituminous coking coals, subbituminous coals, and lignite brown coals. More than 70% of coal resources belong to the brown coals [1]. The Tavan tolgoi and Nariin sukhait deposits are the biggest and most important for the export of Mongolia bituminous coking coals and Baganuur and Shivee-Ovoo deposits are also the biggest and most important for the internal energy system in Mongolia brown coals. The Tavan tolgoi and Nariin sukhait deposits locate in the South Gobi Region and Baganuur and Shivee-Ovoo deposits locate just in the Central Economic Region of Mongolia.

In general, coal undergoes a series of physical and chemical changes during pyrolysis. Various pyrolysis conditions (i.e. coal type, pyrolysis temperature, atmosphere, heating rate, and catalyst factors) significantly affect these physical and chemical changes [2-5]. On the other hand, pyrolysis is an efficient treatment method of organic material at elevated temperatures in the absence of oxygen. It involves the simultaneous change of chemical composition and physical phase during thermochemical decomposition of organic material by heat and is irreversible [6-8]. As a result of pyrolysis, a solid (hard residue), condensed liquid (tar and pyrolysis water), and gas (uncondensed) products can be obtained. From these products, the solid product can be used as coke, semicoke, smokeless fuel, and adsorbent material based on its properties of a porous and higher caloric value. Tar is petroleum-like product and can be used as complex raw material for the production of chemical substances, gasoline, diesel, oils, bitumen, and so on. The gas product can be used as gas fuel after cleaning nitrogen and sulphur-containing pollutants in it [6, 7]. Generally, before the pyrolysis experiments of coal necessary to carry out thermogravimetric analysis to investigate the mechanism of thermal decomposition coal organic mass and to determine the thermal stability characteristics such as thermostability indices (T_5 % and T_{25} %) and to evaluate how are easy for pyrolysis [9,10]. During the last decade, we are working on pyrolysis of some organic raw materials including different rank coals [11, 12], oil shale [13-15], wood waste [16-18], animal bone [19, 20], cedar shell [21], polypropylene waste [22], milk casein [23-25] and characterization of obtained hard residue, tar and gas product after pyrolysis.

The conversion of coal into oil and gas is a major issue in the country, which will affect national safety and economically sustainable development. Therefore, more detailed investigations by using modern instrumental analysis such as FTIR and thermogravimetric analysis and different pyrolytic experimental methods are very important for the future development of coal processing industries in Mongolia. For this reason, the coals of Tavan tolgoi, Nariin sukhait, Baganuur, and Shivee-Ovoo deposits in Mongolia have been chosen the detailed investigation on thermal processing including pyrolysis and characterization of obtained solid (hard residue) and liquid products after pyrolysis.

2. EXPERIMENTAL

2.1. Sample Preparation

Four coals were crushed into small pieces 3-6 mm in size and the analytical sample was prepared by powdering the coal into small particles size < 0.2 mm in a steel mill. Analytical sample preparation (MNS 27192001), proximate and ultimate analysis of coal were performed according to Mongolian National Standards MNS 656-79 (moisture content), MNS 652-79 (ash yield), MNS 654-79 (volatile matter yield).

The elemental composition of coal was determined by microanalytical instrument 5E C2000, model CNH-analyser. The FTIR spectrum of coal was obtained on a Nicolet 20-PC FTIR spectrometer with CsI optics and DTGS detector. The KBr disc contained a 0.5% finely ground coal sample. All the spectra were measured in the frequency range of 4000 to 400 cm^{-1}, and 32 scans were taken for every sample.

2.2. Thermogravimetric Analysis

Thermogravimetric analysis of coal was carried out in TG/DTA7200, (Hitachi, Japan). Conditions of analysis were as follows: Sample weight -5-10 mg. Heating temperature range -20-1150°C, Heating rate -20°C/min, Carrier gas-argon, Crucible made by Pt-Rh.

2.3. Pyrolysis Analysis

Small-scale pyrolysis experiments of coal samples were performed in a laboratory quartz retort (tube) which could process 1 g of coal sample. The retort was placed in a horizontal electric tube furnace. A chrome-alumel thermocouple was immersed in the tube furnace to measure the actual heating temperature. Pyrolysis experiments have been carried out at different temperatures 200-700°C with a constant heating rate of 20°C/min. First of all, the quartz retort with coal sample was heated, for example, to 600°C with a heating rate of 20°C/min, and kept at 700°C for 80 min. The retort was connected with a thermostable glass tube heated also in a tube furnace at 80°C for collecting tar. This tube was also connected with an air-cooled glass vessel for collecting pyrolysed water. The glass vessel for pyrolysed water was connected with a thin glass tube for non-condensable gases. The yields of pyrolysed products, including solid residue (biochar), tar (condensed liquid product), and pyrolysed water were determined by weighing, and the yield of gases was determined based on their differences.

For the collection of more quantities of pyrolysis hard residue and liquid tar products have used a bigger scale pyrolysis apparatus. The vertical cylindrical retort is made of stainless steel in which 1 kg of coal sample can be pyrolized. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 950°C. A chrome-alumel thermocouple was immersed in the coal bed to measure the actual heating temperature with temperature control (potentiometer). The retort was connected with an air-cooled iron tube and the water-cooled laboratory glass condenser and a collection vessel for the condensate of liquid product (pitch and pyrolysis water). The non-condensable gases after water-cooled condenser were left the system through a thin glass tube. The experiments were carried out to a 500°C temperature and the heating rate was 20°C/min. The yields of products including solid residue (coal char), tar, and pyrolysis water were determined by weighing, and the yield of gases by difference.

2.4. Method for Separation of Tar and Pyrolysis Water

The liquid product of coal pyrolysis consists of tar and pyrolysed water. They form unmixed two layers and can be separated easily by separating in a glass funnel. The upper layer is tar (viscous liquid) with black-brown color and an unpleasant smell.

Table 1. The main technical characteristics and ultimate analysis of coal samples

Coal deposits	**Moisture, %**	**Ash, %**	**Volatile matter, %**	**Caloric value, кcal/кg**	**Carbon, %**	**Hydrogen, %**	**Nitrogen, Oxygen and others,%**	**Sulfur, %**
	W^a	A^d	V^{daf}	Q_s^{daf}	C^{daf}	H^{daf}	$(N+O)^{daf}$	S^a
Tavan tolgoi IV am	14.7	0.8	29.9	7524.0	84.0	5.4	10.2	1.0
Nariin sukhait	1.0	15.8	36.9	7685.0	84.9	4.4	10.7	1.6
Shivee-Ovoo	13.4	21.2	41.0	6501.0	71.3	4.9	22.6	1.1
Baganuur	9.4	13.3	47.0	6848.0	70.5	5.7	23.3	0.5

The bottom layer is pyrolysed water (non-viscous liquid) with an unpleasant smell and yellowish in color. The final cleaning of tar was done by mixing with thermally treated $CaCl_2$ and through separation using filtering or centrifuging. The products, yellowish pyrolysed water with a gravity of 0.9227 g/cm^3 and a solid residue with 7.2% were obtained after evaporation at room temperature.

3. RESULTS AND DISCUSSION

We have determined the technical characteristics, ultimate analysis of coal, and inorganic elemental composition of coal ash in four selected coal samples including Tavan tolgoi, Nariin sukhait, Baganuur, and Shivee-Ovoo deposits in Mongolia are show in Table 1. The results of proximate and ultimate analysis of coal samples show that the caloric value and carbon content are higher for the coal samples of Tavan tolgoi and Nariin sukhait deposits than that of Shivee-Ovoo and Baganuur coal deposits. Besides, the contents of volatile matter and oxygen contents of coal samples of Tavan tolgoi and Nariin sukhait deposits are lower than that of Shivee-Ovoo and Baganuur coal deposits. The content of sufur is lower in all coal samples, which is good from an environmental point of view.

We further analzed the coal samples by FTIR analysis for the characterization of coal organic mass Figure 1.

The IR-spectrum (Figure 1) of initial coal samples show that there are absorbtion bands with low intensities characterizing high molecular polymerized material.

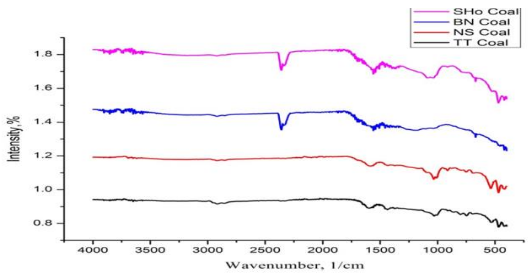

Figure 1. The FTIR spectrum of Tavan tolgoi (TT), Nariin sukhait (NS), Baganuur (BN) and Shivee-Ovoo (ShO) coal

Figure 1 shows that there are lower intensity absorption bands of $-CH_3$, $-CH_2$, -CH groups connected with aliphatic and aromatic radicals at 2800-2900 cm^{-1}, for >CO, -COOH, groups connected with mostly aromatic radicals at 1600 cm^{-1}, for aromatic -CH groups at 1438 and 700-900 cm^{-1}. In the IR spectrum (Figure 1, NS) of Nariin sukhait coal, there are several week absorption bands for -CH aromatic group at 500-750 cm^{-1} and for aliphatic -CH; $–CH_2$ and $–CH_3$ groups with middle intensity at 1249 cm^{-1} and a sharp bands with higher intensity at 2854-2923 cm^{-1}. Also, a strong absorption bands for >C=O groups at 1600 cm^{-1}, week bands for -O- groups at 1400 cm^{-1} and for C-O- groups at 1000-1100 cm^{-1}. Therefore, the coal organic mass of Nariin sukhait coal consists mainly of the aliphatic, aromatic, and aromatic-aliphatic structures with the above-mentioned groups inside.

IR spectrum of Baganuur coal can be recognized following absorption frequency regions:700-900 cm^{-1} for C_{ar}-H; 1000-1300 cm^{-1} for vibration of bonds in various oxygen-containing groups; 1350-1470 cm^{-1} for vibrations of -CH, - CH_2, and -CH_3 groups; 1500-630 cm^{-1} for skeletal vibrations of aromatic rings, >C=O bonds in ketones, aldehydes and quinines. In the IR spectrum (Figure 1, ShO) of Shivee-Ovoo coal, there are several weak absorption bands for the -CH aromatic group at 500-700 cm^{-1}, and for aliphatic -CH -CH_2 and -CH_3 groups with middle intensity at 1250 cm^{-1}. And, a strong absorption band for >C=O groups at 1600 cm^{-1}, weak band for -O- groups at 1400 cm^{-1} and for C-O- groups at 1000-1200 cm^{-1}. Therefore, the coal organic mass of Shivee-Ovoo coal consists mainly of aliphatic, aromatic, and aromatic-aliphatic structures. For investigation of the mineral matter of the four coals have obtained pure ash of each coal after completely burning the analytical coal sample at 950°C and tested it by FTIR analysis (Figure 2) and determined the mineral composition by using Roentgen fluorescence analysis (Table 2).

Table 2. The chemical composition of coals ashes (wt %)

Oxides	**MgO**	**Al_2O_3**	**SiO_2**	**SO_3**	**K_2O**	**CaO**	**TiO_2**	**Mn_2O_3**	**Fe_2O_3**	**CuO**	**PbO**	**P_2O_5**	**Ratio**
TT	-	15.7	77.6	1.9	0.5	1.9	0.9	-	0.7	0.1	-	0.6	0.03
NS	2.5	17.1	22.8	7.3	3.0	14.8	2.7	0.6	27.5	0.1	0.9	0.4	0.4
SHO	4.3	7.2	27.7	19.0	1.1	28.9	1.2	1.6	8.4	-	-	-	1.2
BN	2.6	6.2	24.2	7.2	0.9	40.4	1.2	0.4	17.4	0.1	0.03	-	0.4
Elements	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe	Cu	Pb	P	
TT	-	8.3	36.4	0.8	0.43	1.4	0.6	-	0.5	-	-	-	
NS	1.5	9.0	10.6	2.9	2.5	10.6	1.6	0.4	19.3	0.1	-	-	
SHO	1.5	9.0	10.6	2.9	2.5	10.6	1.6	-	19.3	0.1	-	-	
BN	1.6	0.3	11.3	2.9	0.8	28.9	0.7	0.2	12.2	0.1	-	0.1	

Ratio of oxides - (Fe_2O_3 + CaO + MgO + Na_2O + K_2O) / (SiO_2 + Al_2O_3 + TiO_2)
Acidic (Ac) < 1 < Alcaline (Al)

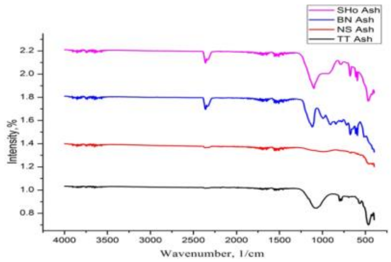

Figure 2. The FTIR spectrum of coal ashes of Tavan tolgoi (TT), Nariin sukhait (NS), Baganuur (BN) and Shivee-Ovoo (ShO) coal

The FTIR spectrum of four coal ashes of Tavan tolgoi (TT), Nariin sukhait (NS-only here is with middle intensity), Baganuur (BN) and Shivee-Ovoo (ShO) deposits in Figure 2 show that the most intensive and the biggest peak at 1150 cm^{-1} belongs for the Si-O- and Ca-O- groups in SiO_2 and CaO which have highest contents than other groups. Besides, there was another peak with middle intensity at 1100 $см^{-1}$ for -O-Al-group in Al_2O_3, and other peaks with lower intensities for -O-Fe-; -O-Mg-groups in Fe_2O_3 and MgO in the coal ash. In the case of Nariin sukhait (NS) coal ash, the most intensive and biggest peak at 1350 cm^{-1} belongs to the -O-Fe-group in Fe_2O_3.

Table 2 show that the coal ash of Tavan tolgoi (TT) deposit has the highest content of elements Si and Al and their oxides SiO_2 and Al_2O_3, in the case of Baganuur (BN) and Shivee-Ovoo (SHO) coal ashes have the highest content of Ca and Si and their oxides CaO and SiO_2. The contents of Fe and Si and their oxides Fe_2O_3 and SiO_2 have the highest contents in the ash of Nariin sukhait (NS) coal, which is different than that of Tavan tolgoi coal ash. The contents of Al, Fe, S, and Mg and their oxides Al_2O_3, Fe_2O_3, SO_3, and MgO have middle contents in the coal ashes of Baganuur and Shivee-Ovoo deposits. Besides, the middle contents have Al, CaO, S, Mg and Ti and their oxides in the Nariin sukhait coal ash and only S and Ca and their oxides in the coal ash of the Tavan tolgoi deposit. All other elements and their oxides determined in the four coal ashes have the lowest contents.

Table 3. The content of radioactive elements in coals and coal ashes

Coal deposit	**The activity of isotopes, Bk/кg**			**The content of radioactive elements**			**Radium equivalent , Bk/kg**
	Ra-226	**Th-232**	**K-40**	**U, g /ton**	**Th, g/ton**	**K, %**	
Tavan tolgoi IV coal	13.4	6.0	460.2	1.1	1.5	1.5	60.4
Tavan tolgoi IV coal ash	8.0	75.2	1203.0	6.4	18.4	4.0	278.9
Nariin sukhait coal	8.0	1.3	29.4	0.7	0.3	0.1	5.5
Nariin sukhait coal ash	67.0	26.0	130.0	5.5	6.3	0.4	110.2

Baganuur coal	85.1	14.8	66.6	13.5	3.6	0.2	148.7
Baganuur coal ash	2025.0	67.0	350.0	163.9	16.5	1.1	580.0
Shivee-Ovoo coal	19.8	8.5	621.2	1.6	2.1	2.1	83.7
Shivee-Ovoo coal ash	106.1	59.3	1177.0	8.7	14.5	3.9	283.1

To determine the character (acidic or alkaline) of each coal ash was calculated the ratio between the following sum oxides: (Fe_2O_3+CaO+MgO+Na_2O+K_2O/SiO_2+Al_2O_3+TiO_2.

If this ratio is less than 1, that coal ash has an acidic (Ac.) characteristic and it is more than 1 the coal ash has an alkaline (Al.) character Table 2.

The contents of radioactive elements in the analytical coal samples and their ashes were determined by gamma spectrometric analysis and the results are given in Table 3.

The contents of radioactive elements in the analytical coal samples of four deposits in Table 3 are lower, but their contents in their ashes increased (enriched) significantly for example the content of U, Th, and Ra 20 increased many times in comparison with initial coal samples.

The thermogravimetric analysis is the most useful method for the investigation of thermal decomposition and thermal stability of natural organic resources including coals. Therefore, the analytical coal samples of selected four coal samples were the object of thermogravimetric analysis and obtained TG curves Figure 3, DTA curves Figure 4, and DTG curves Figure 5.

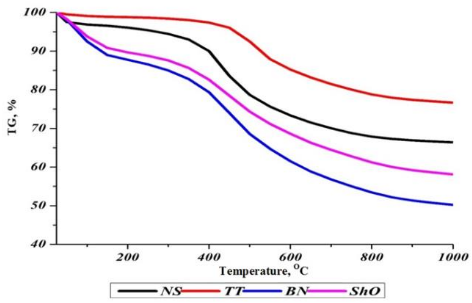

Figure 3. TG curves of Tavan tolgoi (TT), Nariin sukhait (NS), Baganuur (BN) and Shivee-Ovoo (ShO) coal

The heating of four coal samples at temperatures in the range of 25-1020°C in argon atmosphere, with a heating rate of 40°C/min shows that the thermal decomposition of coals ended with about 20.0% weight loss and 80.0% hard residue at 1000°C for Tavan tolgoi coal, with about 32.0% weight loss and 68.0% hard residue at 1000°C for Nariin sukhait coal, with about 38.0% weight loss and 62.0% hard residue at 1000°C for Shivee-Ovoo coal and with about 48.0% weight loss and 52.0% hard residue at 1000°C for Baganuur coal, Figure 3. These results show that the high-rank coals of Tavan tolgoi and Nariin sukhait coals are more thermostable with lower weight loss than that of lower-rank coals of Shivee-Ovoo and Baganuur coals with lower thermal stability. For this reason, three different thermal stability have been determined from each coal sample from the TG curves in Figure 3, Table 4.

Table 4. The thermal stability (T_5 %, T_{15} %, and T_{25} %) of four coal samples

Coal deposits	Thermalstabilty indices, °C		
	T_5 %	T_{15} %	T_{25} %
Baganuur	55.3	159.6	411.2
Shivee-Ovoo	78.8	347.8	434.1
Nariin sukhait	425.3	498.6	620.0
Tavan tolgoi	440.7	529.9	813.7

In the thermal stability results, T_5 % indicates the beginning of thermal decomposition of the coal organic mass, whereas T_{15} % indicates the middle period of thermal decomposition and T_{25} % indicates the ending of thermal decomposition of coal sample. In addition, the thermal stability results show that the high-rank coals of Tavan tolgoi and Nariin sukhait have much higher thermal stability indices than that of lower rank coals of Shivee-Ovoo and Baganuur coals.

Table 5. The determined from the Figure 3 temperature intervals, °C of four coal samples

Coal deposits	The determined temperature intervals, °C			
	I	II	III	IV
Baganuur	25-180	180-380	380-800	800-1000
Shivee-Ovoo	25-180	180-380	380-800	800-1000
Nariinsukhait	25-50	50-390	390-800	800-1000
Tavan tolgoi	25-450	450-800	800-1000	-

As show in Table 5, the steps are different for high rank and low rank coals. These steps are similar for low rank coals of Baganuur and Shivee-Ovoo coals, and however, for Nariin sukhait coal I and II, the steps are much different than that of low rank coals. For the Tavan tolgoi coal, it has even only three steps. Usually, in I step, the weight loss is due to the release of some absorbed gas and moisture from the coal sample. In II step, intensive thermal decomposition of the organic matter of the coal samples start forming liquid (tar and pyrolysis water) and gas products. In III step, the weight loss strongly decreases, which is an indication for ending thermal decomposition and starting carbonization of the coal sample. In IV step, the weight loss lowly increases, which is related to the release of gas, e.g. CO_2, H_2, CO from the mineral matter of coal sample.

The first minimum peak of DTA at 105°C for Baganuur and Shivee-Ovoo coal shows the endothermic reaction process related to the releasing of the adsorbed gas and moisture from the coal sample.

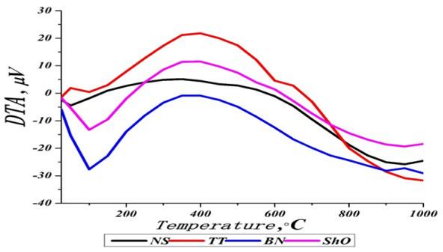

Figure 4. DTA curves of Tavan tolgoi (TT), Nariin sukhait (NS), Baganuur (BN) and Shivee-Ovoo (ShO) coal

A big exothermic reaction peak at 400℃ related to the intensive thermal destruction of the coal organic mass from the sample. Also, the DTA curves of high-rank coals of Tavan tolgoi and Shivee-Ovoo coals are much different than that of low-rank coals of Baganuur and Shivee-Ovoo coals. For example, the DTA curve of Nariin sukhait coal has a very little endothermic minimum.

The DTG curves of four coal samples indicate the first exothermic maximum as the sign of releasing of the moisture and adsorbed gas, and the second big exothermic peak as related to the thermal destruction reactions of coal organic mass with the maximum rate Figure 5.

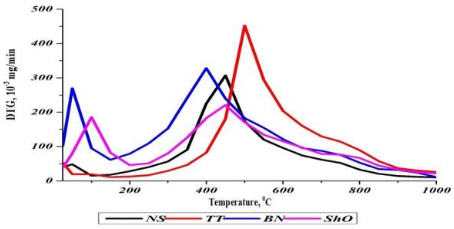

Figure 5. DTG curves of Tavan tolgoi (TT), Nariin sukhait (NS), Baganuur (BN) and Shivee-Ovoo (ShO) coal

The DTG curves differ with different temperature maximum points of exothermic peaks depending on the nature of coal organic mass of each coal samples. Pyrolysis is one method of the used thermal processing of coals to produce a solid (hard residue or semicoke and coke), condensed liquid (tar), and uncondensed gas product. For this reason, the four coal samples were pyrolyzed in a standard quartz retort at different heating temperatures (200℃ -700℃) for 80 min and determined the yields of char, tar, pyrolysis water, and gas Table 6.

Table 6. The yields of pyrolysis products at different heating temperatures

Coal deposits	Heating temperatures,°C	The yields of pyrolysis products, (%)			
		Hard residue	Tar	Pyrolysis water	Gas and loss
Tavantolgoi	200	99.1	-	0.6	0.3
	300	98.8	0.3	0.9	0.3
	400	97.9	0.3	1.3	0.7
	500	92.3	2.5	2.8	2.3
	600	89.6	3.0	2.3	5.2
	700	84.6	3.5	4.4	7.4
	800	78.9	4.0	4.6	12.4
Nariin sukhait	200	99.2	-	0.2	0.5
	300	97.9	0.3	1.1	0.7
	400	95.3	0.7	2.5	1.5
	500	93.0	1.1	3.5	2.5
	600	88.5	2.4	4.0	5.1
	700	83.8	3.6	6.5	6.1
	800	83.3	3.5	5.1	6.1
Baganuur	200	90.0	1.9	3.4	4.7
	300	90.3	0.4	4.0	5.3
	400	76.6	6.6	10.4	6.4
	500	60.3	6.9	14.9	17.9
	600	56.8	7.0	14.8	21.4
	700	59.5	3.5	13.1	23.9
	800	55.5	3.6	6.3	29.0

Shivee Ovoo	200	83.0	0.0	15.8	1.2
	300	77.1	1.1	17.1	4.5
	400	75.3	3.0	17.2	4.5
	500	56.5	6.3	16.8	20.4
	600	48.9	4.2	12.3	34.6
	700	48.3	3.9	11.2	36.6

The yields of pyrolysis products at different heating temperatures of pyrolysis Table 6 show that the yield of the hard residue from high-rank coals of Tavan tolgoi (78.9% at 800℃) and Nariin sukhait (83.3% at 800℃) are higher than that of low-rank coals of Baganuur (55.5% at 800℃) and Shivee-Ovoo (48.3% at 700℃) coal. This indicates that low-rank coals of Baganuur and Shivee-Ovoo coals have given higher yields of tar, pyrolysis water and gas producs during pyrolysis than that of high-rank coals of Tavan tolgoi and Nariin sukhait coal.

The yield of pyrolysis tar chosen as a main product of pyrolysis of four coal samples and according to this the optimum heating temperature of pyrolysis of Tavan tolgoi coal -4.0% at 800℃, Nariin sukhait -3.6% at 700℃, Baganuur -7.0% at 600℃ and Shivee-Ovoo -6.3% at 500℃. This results show that high-rank coals give the increased hard residue and less tar, whereas low-rank coals give more tar and less hard residue after pyrolysis.

The yield of all thermal decomposition products such as liquid and gas products of low-rank coals of Baganuur and Shivee-Ovoo show that there is an intensive thermal decomposition of the coal organic mass with a higher degree of conversion than that of high-rank coals of Tavan tolgoi and Nariin sukhait. As it was mentioned above about the thermal stability of four coal samples that the organic mass of Baganuur and Shivee-Ovo°Characterize with lower thermal stability than that of high rank (bituminous) coals of Tavan tolgoi and Nariin sukhait therefore brown coals of Baganuur and Shivee-Ovoo are more suitable for gasification and liquefaction and high-rank (bituminous) coals of Tavan tolgoi and Nariin sukhait are more suitable for coking and producing of activated carbons.

The solid product (hard residue or semicoke) after the pyrolysis of four coal samples are one of the main product and for example, the hard residue of Baganuur and Shivee-Ovoo coal can be used as smokeless fuel and activated carbon after briquetting and activation and hard residue of Tavan tolgoi and Nariin sukhait coals can be used as a high-quality coke. For this reason, we have determined the main technical characteristics of the hard residue Table 7.

The proximate analysis results of hard residue after pyrolysis of four coal samples in Table 7 show that the volatile matter content decreased significantly. For example, the content of volatile matter of pyrolysis hard residue of Tavan tolgoi coal decreased 3.1 times, of Nariin sukhait coal 6.3 times, of Shivee-Ovoo coal 2.5 times and of Baganuur coal 5.7 times decreased and increased caloric value in comparison with the initial coal characteristics in Table 1.

Table 7. Main technical characteristics of the pyrolysis hard residue of coals

Hard residue	**Main technical characteristics, %**			**Caloric value, Q^{daf}, kcal/кg**
	Moisture, W^a	**Ash, A^d**	**Volatile matters, V^{daf}**	
Tavantolgoi	1.1	20.1	9.5	
Nariinsukhait	0.6	11.5	5.8	8156.0
Baganuur	2.8	13.9	8.3	6802.0
Shivee Ovoo	0.1	27.4	16.2	7337.9

The proximate analysis results of hard residue after pyrolysis of four coal samples in Table 7 show that the volatile matter content decreased significantly. For example, the content of volatile matter of pyrolysis hard residue of Tavan tolgoi coal decreased 3.1 times, of Nariin sukhait coal 6.3 times, of Shivee-Ovoo coal 2.5 times and of Baganuur coal 5.7 times decreased and increased caloric value in comparison with the initial coal characteristics in Table 1. Also, these results show that there was intensive thermal decomposition of coal organic mass of each coal during pyrolysis.

The condensed liquid product usually calls tar which is the main product of pyrolysis of different organic raw materials including coal. Therefore, was decided to characterize the pyrolysis tars of four coal samples. First, all tars were completely removed from the pyrolysis water by centrifuging and drying with thermally treated calcium chloride and filtering. So dewatered tar tested by IR analysis and the FTIR spectra are shown in Figure 6.

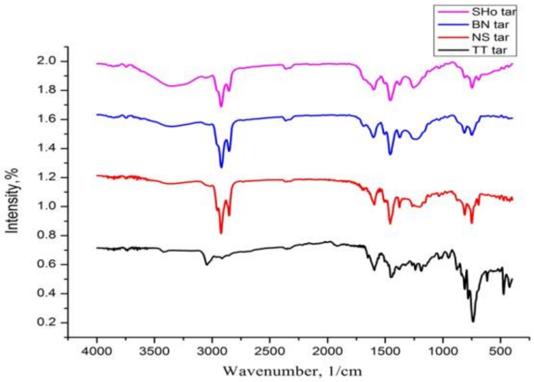

Figure 6. The FTIR spectrum of four pyrolysis tars of Tavan tolgoi (TT), Nariin sukhait (NS), baganuur (BN) and Shivee-Ovoo (ShO) coal

The FTIR spectrum of pyrolysis tars of Tavan tolgoi (TT), Nariin sukhait (NS), Baganuur (BN), and Shivee-Ovoo (ShO) coals are more complicated than FTIR spectra from coal ashes, because they consist of different kinds (classes) of organic compounds with different functional groups and so on. For example, the FTIR spectrum Figure 6 of tar products after pyrolysis were observed the lowest intensity absorption bands for H of aromatic the -CH group at 500-800 cm^{-1} (BN and ShO low-rank coals) and the absorption bands with the highest intensities for H of aliphatic -CH; $-CH_2$ and $-CH_3$ groups at 2850-2947 cm^{-1} for four pyrolysis tars. In the case of pyrolysis tars of high rank coals from Tavan tolgoi (TT) and Nariin sukhait (NS) deposits, the peaks for H of aromatic the -CH groups at 500-1000 cm^{-1} are with middle intensities compared with the that of low-rank coal pyrolysis tars from Baganuur (BN) and Shivee-Ovoo (ShO) coals.

Also, there are absorption bands with the middle intensity for O containing groups such as for the >C=O groups at 1593 cm^{-1}, for -O- groups at 1454 cm^{-1} and the -OH groups at 3000-3300 cm^{-1}. Therefore, the tar product of coals after pyrolysis consist of mainly the aliphatic, aromatic and aromatic-aliphatic compounds with above mentioned functional groups in their molecules.

The chemical composition of each pyrolysis tar determined by chemical analysis in group organic compounds and the results are given in Table 8.

The results in Table 8 show that the neutral oils are the main component with the highest content and asphaltenes, free carbons are with middle content.

The contents of organic bases, organic acids, and phenols are the lowest. As mentioned above, organic bases and organic acids were removed from the pyrolysis tar of coals and so purified tar is called a “neutral oil’’.

The chemical composition of the pyrolysis tar in group organic compounds shows that the tar consists of mainly neutral oils and asphaltenes, and organic bases, organic caids and phenolic compounds are in little amounts. The purified pyrolysis tars were distilled at atmosphere and obtained several fractions with different boiling temperature ranges and the yield of fractions are given in Table 9.

Table 8. The chemical composition of the pyrolysis tar in group organic compounds

Coal deposits	The chemical composition of the tar , %					
	Free carbons	Organic bases	Organic acids	Phenols	Asphalteins	Neutral oils
Tavan tolgoi	13.5	0.9	0.9	2.9	16.3	65.4
Nariin sukhait	2.6	1.0	2.5	3.0	2.4	85.0
Baganuur	16.1	2.5	1.7	11.9	16.1	51.7
Shivee-Ovoo	3.9	0.2	0.1	5.8	13.1	76.9

Table 9. The yields of fractions of pyrolysis tar of four coals with different boiling temperature ranges, °C

Coal deposits	Boiling temperature range of fraction, °C	The yield of fraction,%	Discription of fraction
Nariin sukhait	untill 180	1.7	Light fraction (liquid)
	180-250	6.2	Middle fraction (liquid)
	250-320	12.1	Middle fraction (liquid)
	320<	6.5	Heavy fraction (liquid)
	Hard residue	73.5	Hard
	Gas and loss	0	Gas
Baganuur	untill 180	0.8	Light fraction (liquid)
	180-220	33.1	Middle fraction (liquid)
	220-250	48.7	Heavy fraction (liquid)
	Hard residue	17.4	Gas

Shivee-Ovoo	untill 180	15.9	Light fraction (liquid)
	180-320	15.4	Middle fraction (liquid)
	320<	44.5	Heavy fraction (liquid)
	Gas and loss	24.1	Gas
Tavan tolgoi IV	untill 140	0.2	Light fraction (liquid)
	140< hard residue	99.8	Hard
	Gas and loss	0.04	Gas

Table 9 shows that the main product of the distillation of the pyrolysis tars of four coal samples is the heavy fractions, followed by light and middle fractions with different boiling temperature ranges. Only the pyrolysis tar of Tavan tolgoi coal is a very viscous bitumen-like product at room temperature and therefore it's had 99.7% hard residue and very little amount of light fraction and gas products and without middle and heavy fractions. After removing the toxic organic compounds such as organic bases, organic acids, and phenols these fractions can be used as gasoline (light fractions), diesel (middle fractions), and oil products (heavy fractions).

4. CONCLUSION

In the conclusion, the thermal stability indices from high-rank coal of Tavan tolgoi and Nariin sukhait were much higher than that of lower rank coals of Shivee-Ovoo and Baganuur coals. The yields of pyrolysis products at different heating temperatures showed that the yields of hard residue from Tavan tolgoi and Nariin sukhait are also higher than that of coals from Baganuur and Shivee-Ovoo coal. Importantly, the mineral composition analyses showed that the ashes of high-rank coals from Tavan tolgoi and Nariin sukhait deposits have an acidic character whereas the ashes of low-rank coals of Baganuur and Shivee-Ovoo deposits have the alkaline characteristics.

Moreover, the chemical composition of the pyrolysis tar of Tavan tolgoi, Nariin sukhait, Baganuur, and Shivee-Ovoo coals showed that the pyrolysis tar consists mainly of neutral oils, asphaltenes, organic bases, organic acids, and phenolic compounds. The proximate analysis of the pyrolysis hard residue from four coal samples revealed that the volatile matter contents in these samples were decreased significantly. Besides, our study primarily reports the detailed physic-chemical characteristics of the pyrolysis hard residues from the analyzed four coal samples in comparison to the initial coal samples.

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