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Investigation on characterization and liquefaction of coals from Tavan tolgoi deposit

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Abstract: On the basis of proximate, ultimate, petrographic and IR analysis results have been confirmed that the Tavan tolgoi coal is a high-rank G mark stone coal. The results of X-ray fluorescence analysis of coal ash show that the Tavan tolgoi coal is a subbituminous coal. The ash of Tavan tolgoi coal has an acidic character. The results of pyrolysis of Tavan tolgoi coal at different heating temperatures show that a maximum yield - 5.0% of liquid product can be obtained at 700^{0}C. The results of thermal dissolution of Tavan tolgoi coal in tetralin with constant mass ratio between coal and tetralin (1:1.8) at 450^{0}C show that 50.0% of liquid product can be obtained after thermal decomposition of the COM (coal organic matter).

Keywords: coal, pyrolysis, petrographic analys, mineral compounds, thermal dissolution

INTRODUCTION

Coal is the major energy source and feedstock of chemical industry among fossil resources in the coming century because of its abundant reserves and easy availability. Because of instability on world oil market, the diversification of energy carriers is practically implemented in many countries with involvement of various nontraditional types of organic raw materials, primarily, coal, whose reserves are much greater than oil and gas reserves. Mongolia is the country of lack of oil source with relative rich in coal resource. Mongolia has 20 billion tons of proven coal reserves and estimated resources totalling 163 billion tons, mostly of them is low-rank brown coal, but remains undeveloped due to a lack of infrastructure. Such reserves include the huge Tavan tolgoi deposit in the South Gobi, which contains over 6.4 billion tons of high quality stone and coking coal, but lies more than 400 km from the nearest railway. There is a large brown coal basin (Jurassic origin), which contains the Baganuur, Ovdogkhudag, Aduunchuluun, Tevshiin govi, Khoot, Tsaidam nuur and Shivee ovoo deposits and this is located in the central economic region of Mongolia [1]. The most important features of these deposits are accessed by opencast mining and coal can be transported using the nearby railway. In Mongolia coal is currently the main energy carrier for thermal power plants and local boiler houses and there is almost no other form of large-scale coal utilization industry [2].

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Now Mongolia exports about 15 million tons raw coal by trucks from the South gobi to China. However, coal samples from the Tavan tolgoi deposit have been assessed for benefication [3] and coke production [4], samples from Baganuur, Bayanteeg and Shivee ovoo deposits as fuel for pyrolysis [5], hydrogenation [6] and gasification [7, 8]. Also samples from Ovdogkhudag and Aduunchuluun deposits have been assessed for their liquefaction potential using facilities in Japan [9].

At present time Mongolian government pays much more attention for the future development of coal processing industries such as coal benefication, coking, semicoking, gasification and liquefaction. There are already established several small scale semicoking factories in Ulaanbaatar and in Darkhan for production of smokeless fuel. The "Energy Resourses" Company built a middle- scale coal washing factory in South gobi. Mongolian government is planning to establish a coking factory in the framework of "Sainshand" industrial park and "MAK" company a coal liquefaction factory on basis of Aduunchuluun coal deposit.

How to convert coal into oil and gas is a major issue in the country, which will affect the national safety and the economic sustainable development. Therefore more detailed investigation of above mentioned most important coal deposits by using of modern instrumental analysis such as petrographic and different pyrolysis experimental sets is very important for the future development of coal processing industries in Mongolia.

EXPERIMENTAL

The type, resource and other information of the coals of Tavan tolgoi deposit are given in Table 1. The analytical samples of coals from these 2 deposits were prepared according to Mongolian National Standards (MNS) and main technical specifications including moisture (MNS 656-79), ash (MNS 652-79), volatile matter (MNS 654-79), caloric value (MNS 669-87), sulphur content (MNS 895-79) have been determined.

Table 1. Some informations about coal samples of Tavan tolgoi deposit

Name of deposit	Type	Location of the coal deposit	Approx. resources in million ton	Discovered in
Tavan tolgoi	High rank bituminous and coking coal	Tsogttsetsi village of Southgobi aimak,14 km from the Tsogttsetsi soum to the south and 600 km from Ulaanbaatar to the South gobi	Geological reserves 6.4 billion tones	In 1966

The pyrolysis experiments of coal samples were performed in a laboratory small quarts retort (tube) which could contain air dried and powdered to a particle size < 0.2 mm 1 g- of coal sample. The retort was placed in a horizontal electric tube furnace with a maximum heating temperature of 950^{0}C. A chrome-alumel thermocouple was immersed in the tube furnace to measure the actual heating temperature.The pyrolysis experiments have been carried out at different heating temperatures 200 - 800^{0}C with constant heating rate 20^{0}C/min. First of all the quarts retort with coal sample was heated for example to 600^{0}C with heating rate 20^{o}C/min. and kept at 600^{0}C for 80 min. The retort was connected with a thermostable glass tube heated also in a tube furnace at 80^{0}C for collecting of tars and this tube is also connected with a air-cooled glass vessel for collecting of pyrolysis water. The glass vessel for pyrolysis water is also connected with a thin glass tube for non-condensable gases [10].

The yields of pyrolysis products including solid residue (coal char), tar (condensed liquid product) and pyrolysis water determined by weighing, and the yield of gases by differences.

For petrographic studies samples were embedded in a resin, ground flat and polished. All samples were cuttings which were embedded without any specific orientation. Vitrinite reflectance was measured following the standard procedures [11]. It was attempted to measure 50 particles per sample. In addition, fluorescence microscopy was used for rapid qualitative information on maturity and organofacies. Resedimented vitrinite particles are characterized by higher reflectivity than autochthonous vitrinite. Usually, only the vitrinite population with the lowest reflectance values is measured and reported.

For the determination of mineral content in both coals have been obtained completely burned ashes of coals during slowly and continuously burning in furnace at 200 - 850^{0}C. The content of mineral elements in both coal samples and their oxides have been determined by using of X-ray fluorescence spectrometry. The thermal dissolution of coal samples have been carried out in a laboratory standard stainless steel autoclave by using tetralin as a hydrogen donor solvent. Air dried for 24 h, and powdered to a particle size < 0.2 mm 1g coal sample mixed with 1.8g tetralin (mass ratio 1:1.8) in autoclave and heated in a laboratory furnace at temperatures of 350, 400, 450^{o}C for 2 h. After completion of experiment the autoclave with sample cooled at room temperature and removed all uncondensed gas and resulting liquid products were filtered, and the solid residue on filter was subjected to sequential extraction with chloroform in a Soxhlet apparatus. An extract of liquid products of thermal dissolution of coal in tetralin was distilled by a laboratory rotary evaporation apparatus for complete removing of chloroform. The degree of coal conversion was determined from the loss of the organic matter of coal (OMC) after extraction and also change in the ash contents of the initial coal samples and the insoluble residue.

RESULTS AND DISCUSSION

The results of ultimate and proximate analysis of coal samples of boreholes no.4 and 8 from Tavan tolgoi deposit are shown in Table 2.

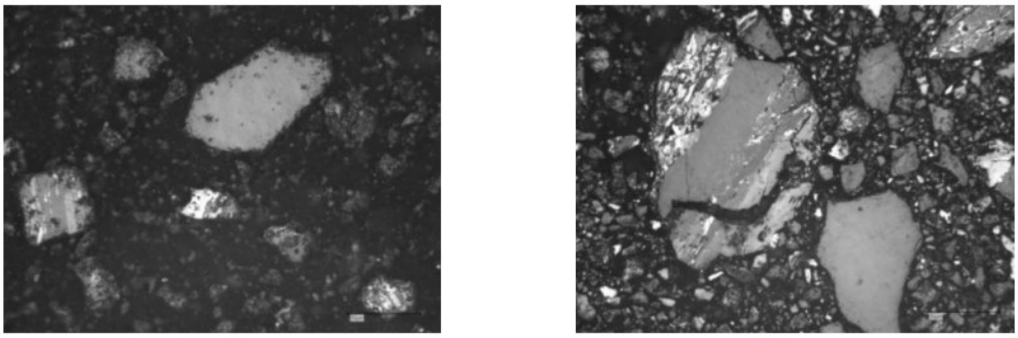
The technical characteristics of Tavan tolgoi coals in Table 2 show that the content of ash in borehole VIII is higher than in borehole IV. The content of sulfure in Borehole VIII is a little bit higher than in Borehole IV and in generally both are comparatively lower which is good for environmental point of view.

Table 2. Proximate and Ultimate analyses of Tavan tolgoi coals

Coal samples of Tavan tolgoi	Proximate analysis, %				Ultimate analysis, %			
	W^a	A^d	V^{daf}	Q^{daf}	S_{total}	C^{daf} %	H^{daf} %	$(N+O)^{daf}$, %
Borehole IV	0.82	14.8	29.9	7524	0.98	84.0	5.42	10.25
Borehole VIII	0.94	18.4	35.7	7283	1.4	76.0	4.40	19.17

Also the content of volatile matter in Borehole IV is lower and caloric value is higher than in Borehole VIII. It means that the coal of Borehole IV has a characteristic of a higher quality than Borehole VIII. The content of C is higher and O is lower in Borehole IV coal than in Borehole VIII.

First time these two coal samples have been characterized with petrographic analysis by microscopic photograph of specially prepared and polished samples and the petrographic photographs (two photographs from each samples) are presented in Figure 1.



A B

Fig. 1. The petrographic photographs of polished coal samples of Tavan tolgoi deposit: Photograph of coal from borehole IV; B- photograph of coal from borehole VIII.

There are clearly indicated bright segments (parts) in the petrographic photographs of two coal samples (Figure 1, A, B) which is the specific petrographic characteristic of vitrinite maceral groups in the organic maturity of the high-rank coal. The next step of petrographic analysis is to measure the value of so called vitrinite reflectance (%R_{Vt}) of points as much as possible on these bright segments (parts) in the petrographic photographs. We have chosen about 50 points on more bright pattern of these photographs and the measured results of %R_{Vt} are given in Table 3 and 4.

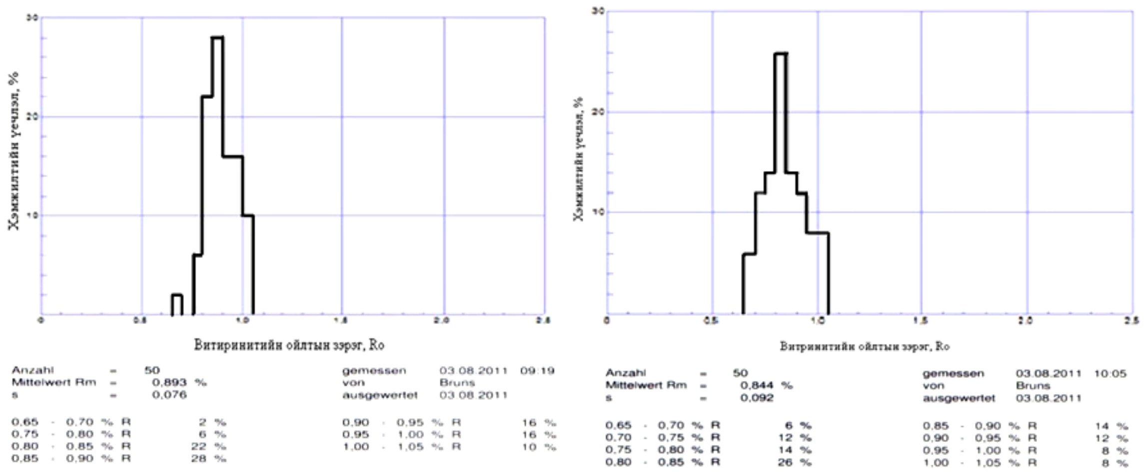
Table 3. The measured results of %R_{Vt} from the petrographic patterns of borehole IV coal samples.

№	Ref, %	Time	№	Ref, %	Time
1	0.872	28.9	26	1.004	285.6
2	0.891	32.8	27	1.007	287.8
3	0.838	127.8	28	0.998	289.8
4	0.659	130.5	29	0.875	292.0
5	0.755	133.5	30	0.870	338.7
6	0.876	146.2	31	0.834	342.9
7	0.931	148.7	32	0.801	348.9
8	0.831	151.5	33	0.822	350.5
9	0.856	157.5	34	0.890	353.9
10	0.943	179.5	35	0.951	355.9
11	0.848	181.1	36	0.948	357.8
12	0.761	183.2	37	0.957	359.3
13	0.847	186.5	38	0.904	361.8
14	0.953	210.6	39	0.890	422.0
15	0.941	213.7	40	0.897	425.1
16	0.965	216.4	41	0.883	426.3
17	1.022	221.0	42	0.828	428.0
18	1.016	223.9	43	0.835	430.5
19	0.988	226.4	44	0.880	433.2
20	0.958	228.7	45	0.902	449.0
21	0.890	230.5	46	0.809	451.7
22	0.971	232.7	47	0.873	453.5
23	0.886	235.9	48	0.849	454.2
24	0.910	240.9	49	0.773	455.0
25	1.047	283.7	50	0.899	457.5

Table 4. The measured results of $\%R_{Vt}$ from the petrographic patterns of borehole VIII coal samples.

№	Ref, %	Time	№	Ref,%	Time
1	0.843	74.7	26	0.731	295.3
2	0.680	77.6	27	0.932	320.1
3	0.749	80.0	28	0.969	322.2
4	0.724	83.6	29	1.005	323.3
5	0.904	120.9	30	0.990	325.3
6	0.917	123.2	31	1.006	329.4
7	0.855	125.0	32	0.917	339.9
8	0.851	127.4	33	0.891	377.8
9	0.836	128.7	34	0.927	379.8
10	0.863	129.6	35	0.936	383.7
11	0.814	131.1	36	1.030	399.1
12	0.875	132.6	37	0.740	428.8
13	0.821	143.2	38	0.735	446.6
14	0.813	145.6	39	0.670	448.4
15	0.812	149.8	40	0.830	462.6
16	0.773	152.5	41	0.875	464.6
17	0.791	163.9	42	0.815	465.6
18	0.822	278.1	43	0.835	467.4
19	0.751	280.0	44	0.814	468.1
20	0.772	280.9	45	0.853	510.5
21	0.782	283.2	46	0.847	512.4
22	0.746	285.1	47	0.792	519.7
23	0.792	287.2	48	1.009	527.8
24	0.809	289.7	49	0.985	537.2
25	0.677	292.7	50	0.974	537.8

The measured results of $\%R_{Vt}$ from the petrographic patterns of 2 coal samples in Table 3 and 4 are summarized and shown as a diagrams (Figure 2) for determination of averaged value of $\%R_{Vt}$ for each coal samples.



A B

Fig. 2. The diagrams for determination of averaged value of $\%R_{Vt}$ for coal of Tavan tolgoi deposit: A – for borehole IV; B - for borehole VIII.

From the Fig. 2 have been determined the averaged value of $\%R\ V_t$ for coal of borehole IV(A) is 0.893% and for coal of borehole VIII (B) is 0.844%.

The determined averaged vitrinte reflectance ($\%R_{Vt}$) of each coal samples confirm that the Tavan tolgoi coal has a characteristic ($\%R_{Vt}$ = 0.893% - 0.844%) of high-rank G mark coking coal [10 P.157].

For the characterization of two coals from Tavan tolgoi deposit have been carried out IR analysis of each coal samples (IR spectra of borehole IV coal in Figure 3 and IR spectra of borehole VIII coal in Figure 4).

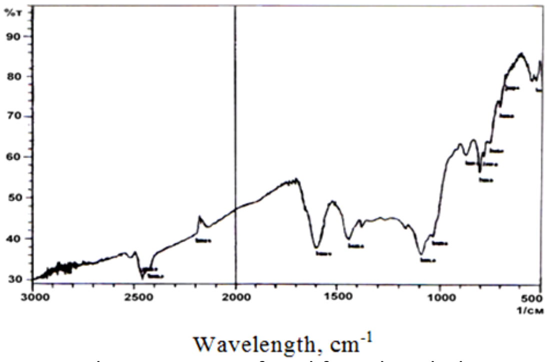


Fig. 3. The IR spectra of coal from borehole IV

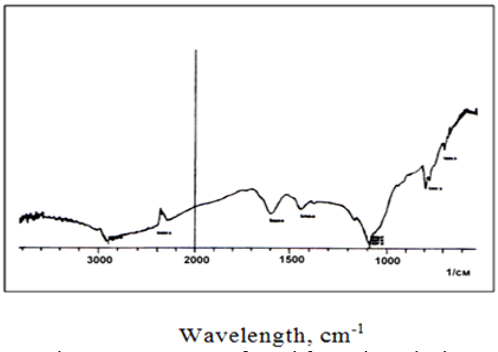


Fig. 4. The IR spectrum of coal from borehole VIII

In the IR spectra of coal from borehole IV and VIII 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 - 1630cm^{-1} for skeletal vibrations of aromatic rings, >C=O bonds in ketones, aldehydes and quinines; 2800 - 2950 cm^{-1} for stretching vibrations of –CH. -CH_2 and – CH_3 groups in saturated aliphatic structures; and 3030 -3350 cm^{-1} for stretching associated vibrations of – OH groups in aromatic rings and aliphatic structures. The both IR spectra are similar. In the case of Tsaidamnuur coal IR spectra have very week and continous absorption bands (the absorption bands are not sharp).

The content of mineral elements in both coal samples and their oxides has been determined by using of X-ray fluorescence spectrometry and the results are shown in Figure 5 and 6 and Table 5.

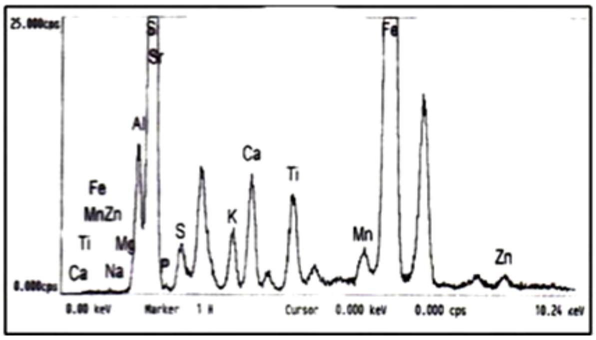


Fig. 5. The X-ray fluorescence spectrogram of coal coal ash of VIII from Tavan tolgoi deposit

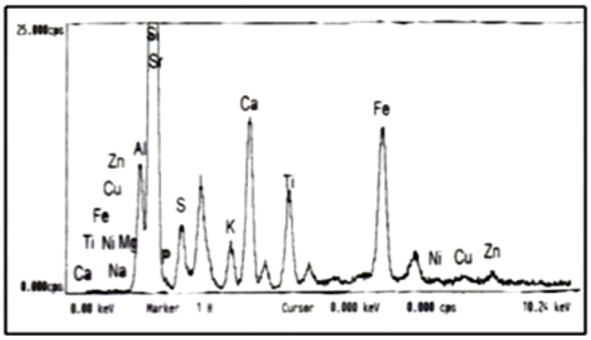


Fig. 6. The X-ray fluorescence spectrogram of ash of IV from Tavan tolgoi deposit

The dates in Figure 5 - 6 and Table 4 show that highest content of elements have Si, O and SiO_2 in coal ash of both samples of Tavan tolgoi deposit. In the case of Al, Fe, Ca, S and Al_2O_3, Fe_2O_3, CaO, SO_3 their contents are in a middle position in both samples. Lowest contents have K, P, Ti, Mn, Zn, Sr and their oxides in both coal ashes. The sum of CaO and MgO ($CaO+MgO<Fe_2O_3$=6.103-7.180) and the ratio ($Fe_2O_3+CaO+MgO+Na_2O+K_2O$)/ ($SiO_2+Al_2O_3+TiO_2$)<1in both coal ash samples show that the Tavan tolgoi coal is a high rank subbituminous coal and it's ash has an acidic character.

Table 4. The mineral composition of coal ash of Tavan tolgoi deposit

№	Elements, %	Elements, %	Borehole VIII	Oxides,%	Borehole IV	Borehole VIII
1	Na	0.000	0.000	Na_2O	0.000	0.000
2	Mg	0.000	0.000	MgO	0.000	0.000
3	Al	8.337	9.898	Al_2O_3	15.753	18.703
4	Si	36.281	33.075	SiO_2	77.611	70.755
5	P	0.252	0.130	P_2O_5	0.578	0.299
6	S	0.774	0.482	SO_3	1.934	1.203
7	K	0.430	0.552	K_2O	0.518	0.665
8	Ca	1.348	0.844	CaO	1.886	1.180
9	Ti	0.553	0.535	TiO_2	0.923	0.893
10	Fe	0.502	4.268	Fe_2O_3	7.180	6.103
11	Ni	0.009	-	NiO	0.012	-
12	Cu	0.011	-	CuO	0.014	-
13	Zn	0.021	0.034	ZnO	0.027	0.043
14	Sr	0.023	0.009	SrO	0.028	0.011
15	Mn	-	0.101	Mn_2O_3	-	0.145
16	O	51.458	50.070		-	

As it is known that subbituminous coals are useful raw material for a liquefaction technologies. The pyrolysis and thermal dissolution (hydrogen-donor solvent refining) are two different process of liquefaction for production of petroleum like liquid product (as main product) from solid fossil fuels.
For this reason coals from Tavan tolgoi deposit have been tested for a pyrolysis experiments aimed to determine an optimal heating temperature of coals in absent of oxygen and the determination of the yield of tar (liquid condensed petroleum like product) are chosen as the most important characteristic. The yields of pyrolysis products of borehole IV (Table 6) and of borehole VIII (Table 7) from Tavan tolgoi coals including hard residue, tar, pyrolysis water and gas after pyrolysis experiments at different temperatures of heating and constant heating rate (20^0C/min) are given in Figures 7 and 8.

Table 6. The yields of pyrolysis products of borehole IV from Tavan tolgoi coals

Sample	T ^{0}C	t [min]	Hard residue, %	Tar, %	Pyrolysis water, %	Gas and loss, %
Borehole IV	200	80	99.09	-	0.6	0.3
	300	80	98.76	0.31	0.9	0.03
	400	80	97.86	0.33	1.32	0.75
	500	80	92.29	2.53	2.86	2.32
	600	80	89.6	2.89	2.32	5.19
	700	80	84.58	3.5	4.4	7.4
	800	80	78.9	4	4.61	12.4

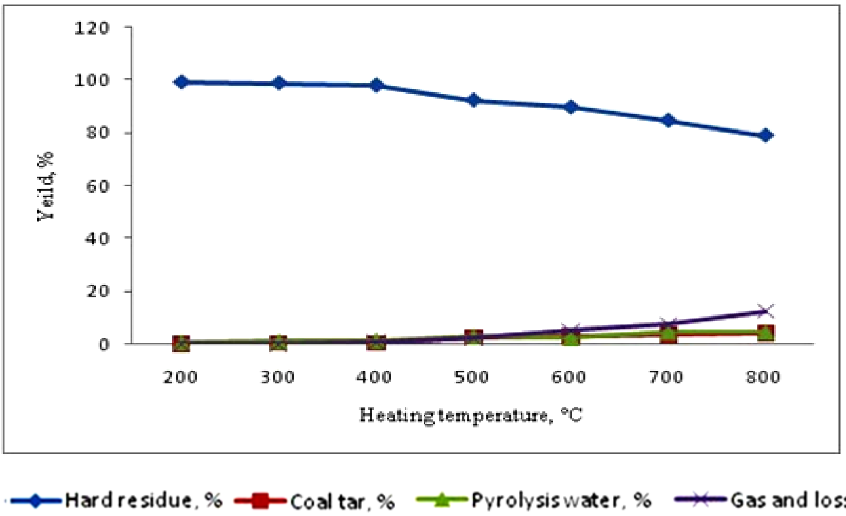


Fig. 7. The yields of pyrolysis products of borehole IV from Tavan tolgoi coal at different heating temperature

The yields of pyrolysis products of borehole IV and VIII from Tavan tolgoi coal at different heating temperature in Table and Figure and the results are very similar in both cases and show that the yield of hard residue is decreased by increasing of heating temperatures, because of increasing thermal decomposition of organic matter of coal at higher temperature.
The yield of main product (tar) of pyrolysis of both coal from Tavan tolgoi deposit increasing by the heating temperature until 700^0C in which has a highest yield 4 - 5% which is lower than that of brown coal. Also, as usually the yields of pyrolysis water and uncondensed gases increased by increasing of heating temperatures.

Table 7. The yields of pyrolysis products of borehole VIII from Tavan tolgoi coals

Sample	T^{0}C	t [мin]	Hard residue, %	Tar. %	Pyrolysis water, %	Gas and loss, %
Borehol e VIII	200	80	98.92	-	1.33	0.25
	300	80	97.13	0.196	2.0	0.65
	400	80	97.14	0.4	1.54	0.9
	500	80	90.18	1.44	3.42	4.94
	600	80	85.65	3.57	3.04	7.72
	700	80	81.27	4.77	3.55	10.4
	800	80	69.28	4.45	5.48	15.77

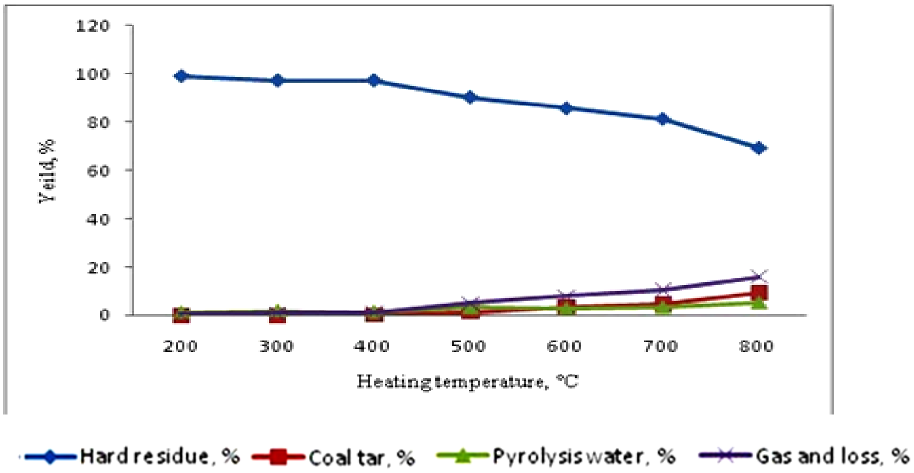


Fig. 8. The yields of pyrolysis products of borehole VIII from Tavan tolgoi coal at different heating temperature

All above mentioned experimental results of boreholes IV and VIII coal samples from Tavan tolgoi deposit show that the coal of borehole IV from Tavan tolgoi deposit characterizes with better results (more qualitative) than that of borehole VIII. Therefore the coal sample of borehole IV from Tavan tolgoi deposit was chosen for next thermal dissolution experiments.
The results of pyrolysis experiments of both coal samples from Tavan tolgoi deposit show that these coals can be easily tested for thermal dissolution in tetralin as a hydrogen donor solvent. The results of thermal dissolution of coal of borehole IV from Tavan tolgoi is presented in Figure 9. The yields of thermal dissolution products: hard residue, liquid and gas of this chosen Tavan tolgoi coal sample (Figure 9) at different heating temperatures show that the yield of hard residue is decreasing intensively against the increasing of heating temperatures, because of higher degree of thermal decomposition of coal organic matters at higher temperature.

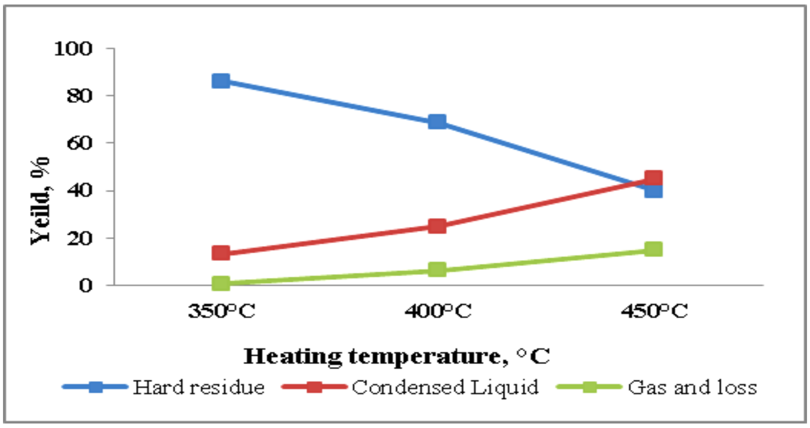


Fig. 9. The yields of thermal dissolution products of Tavan tolgoi coal (borehole IV) at different heating temperatures

A confirmation of this the summarized yields of liquid and gas productions after thermal dissolution should increased, because of increasing weight loss of initial coal sample before the thermal dissolution process. Such dependences already have observed in Fig. 9 and the maximum yield of liquid product is 50.0% at 450^{0}C. The results of thermal dissolution of Tavan tolgoi coal in tetralin with constant mass ratio between coal and tetralin (1:1.8) at 450^{0}C show that 50.0% of liquid product can be obtained after thermal decomposition of the COM (coal organic matter).

CONCLUSIONS

1. On the basis of proximate, ultimate, petrographic and IR analysis results have been confirmed that the Tavan tolgoi coal is a high-rank G mark stone coal.
2. The results of X-ray fluorescence analysis of coal ash show that the Tavan tolgoi coal is a subbituminous coal. The ash of Tavan tolgoi coal has an acidic character.
3. The results of pyrolysis of Tavan tolgoi coal at different heating temperatures show that a maximum yield - 5.0% of liquid product can be obtained at 700^{0}C.

4. The results of thermal dissolution of Tavan tolgoi coal in tetralin with constant mass ratio between coal and tetralin (1:1.8) at 450^0C show that 50.0% of liquid product can be obtained after thermal decomposition of the COM (coal organic matter).

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