Mongolian Academy of Sciences

Mongolian Journal of Chemistry

The Institute of Chemistry & Chemical Technology

Thermal processing of Khoot coal and characterization of obtained solid and liquid products

S.Batbileg, B.Purevsuren*, Ya.Davaajav, J.Namkhainorov

Institute of Chemistry and Chemical Technology, MAS, Peace ave., Ulaanbaatar 13330, Mongolia

Abstract: The coal of Khoot deposit have been investigated and determined the technical characteristics, elemental and petrographical maceral compositions. On the basis of proximate, ultimate, petrographic and IR analysis results have been confirmed that the Khoot coal is a sub-bituminous coal. The hard residue after pyrolysis have been activated by heated water steam and determined the iodine and methylene blue adsorption of initial coal and activated carbon samples from pyrolysis hard residue. The porosity structure of initial coal, activated carbon of pyrolysis hard residue and hard residue after thermolysis (thermal dissolution) have been determined by SEM analysis. The liquid tar product of thermolysis of Khoot coal was investigated by FTIR, ^{13}C and ^{1}H NMR spectrometric analysis. The results of thermolysis of Khoot coal in tetralin with constant mass ratio between coal and tetralin (1:1.8) at 450°C show that 60.8% of liquid product can be obtained after thermolysis of the coal organic mass.

Keywords: coal, petrographic analysis, pyrolysis, thermolysis, activated carbon, tar.

INTRODUCTION

Coal is one of the most important energy sources, especially for power generation and the global coal demand is projected to grow further in the next years [1]. Apart from coal as primary energy fuel, different products such as metallurgical coke, coal tar, synthetic gases can be derived and manufactured from coal, which represent an important feedstock for chemical industry. Compared to oil and natural gas, coal resources are more evenly distributed worldwide and often readily accessible e.g. by surface mining. Because of instability of the world oil market, the diversification of energy carriers is practically implemented in many countries with involvement of various non traditional types of organic raw materials, primarily, coal, whose reserves are much greater than oil and gas reserves [1].

Mongolia is a country which lacks large oil resources but is relative rich in coal resources. Mongolia has estimated coal reserves of 2.5 Gt and estimated resources totalling more than 160 Gt. Most of Mongolia's coal resources is low-rank brown coal, which is undeveloped due to a lack of infrastructure. Such resources include the huge Tavantolgoi deposit in the South Gobi, which contains over 6.4 Gt of high quality hard coal and coking coal, but lies more than 400 km from the nearest railway. Coal reserves mostly occur in a large brown coal basin (Jurassic origin) located in the central economic region of Mongolia, which contains the Baganuur, Ovdogkhudag, Aduunchuluun, Tevshiingovi, Khoot, Tsaidamnuur and Shiveeovoo deposits [2].

The most important features of these deposits are accessibility by opencast mining and easy transportation using the nearby railway. In Mongolia coal is currently the main energy source for thermal power plants and local boiler houses and there is almost no other form of large-scale coal utilization industry [3]. Presently, almost all of Mongolia's hard coal production (27 Mt in 2011) is exported by trucks from the South Gobi to China.

Coal samples from the Tavantolgoi deposit have been assessed for benefication [4] and coke production [5], samples from Baganuur, Bayanteeg and Shiveeovoo deposits for pyrolysis [6], hydrogenation [7] and gasification [8, 9]. Also samples from Ovdogkhudag and Aduunchuluun deposits have been assessed for their liquefaction potential using facilities in Japan [10]. However, coal of Khoot deposits has not been investigated.

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

*corresponding author: *bpurevsuren.icct@gmail.com*

will utilize coal from the Aduunchuluun deposit.

The conversion of 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 investigations of above mentioned most important coal deposits by using of modern instrumental analysis such as petrographic and different pyrolytic experimental methods is very important for the future development of coal processing industries in Mongolia. For this reason the coal of Khoot deposit has been chosen for the first time detailed investigation on thermal processing including pyrolysis and thermal dissolution (thermolysis), characterization of obtained solid (hard residue) and liquid products.

Coal of Khoot deposit is exploited in an open cast mine since 1980. It is located in the territory of Bayanjargalan village Dundgobi aimak about 450 km to the South from Ulaanbaatar in the Central economic region of Mongolia. Now the Khoot coal mine belongs to the *MAK* company.

EXPERIMENTAL

About 50 kg coal sample was taken by hand collecting different size coal pieces from the newly opened coal seam exploiting for local demands (MNS 2732: 2001). Sample preparation, proximate and ultimate analysis of coal from the Khoot deposit were performed according to Mongolian National Standards MNS 656-79 (moisture content), MNS 652-79 (ash yield), MNS 654-79 (volatile matter yield), MNS 669-87 (gross calorific value) and MNS 895-79 (sulphur content).

Petrographic analysis was performed on polished particulate mounts following recommendations by the International Committee for Coal and Organic Petrology (ICCP) [11]. Vitrinite reflectance was measured using an Axio Imager M2m microscope (Zeiss, Germany) and Fossil software (Hilgers, Germany) on 50 individual vitrinitemacerals in random mode. 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. Maceral group analysis was performed using the same microscope and software by point counting of 500 individual macerals.

The pyrolysis experiments of coal samples were performed in a laboratory vertical cylindrical retort made by stainless steel which could contain 1000 g of sample. 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 and an equipment for temperature control (potentiometer). The retort was connected with a air-cooled iron tube and 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 900°C temperature and the heating rate was 20°C min^{-1}. The yields of products including solid residue (coal char), tar and pyrolysis water determined by weighing, and the yield of gases by difference.

The thermolysis of coal samples was carried out in a stainless steel autoclave using tetralin as a hydrogen donor solvent. Prior to the treatment coal samples were air dried for 24 h, powdered to a particle size < 0.2 mm. Then 1 g coal sample was mixed with 1.8 g tetralin (mass ratio 1:1.8), sealed in the autoclave and heated in a laboratory furnace for 2 h to temperatures of 350°C, 400°C, and 450°C. After completion of each experiment, the autoclave was cooled to room temperature and all uncondensed gas and resulting liquid products were removed, filtered, and the solid residue from the filter was subjected to sequential extraction with chloroform in a Soxhlet apparatus. An extract of liquid products of thermolysis 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 coal organic matter (COM) after extraction and also change in the ash contents of the initial coal samples and the insoluble residue. The yields of pyrolysis products including solid residue (coal char), tar (condensed liquid product) and pyrolysis water were determined by weighing, and the yield of gases calculated by difference.

The pyrolized coal samples (10 - 15 g) have been replaced in quarts tube and flowed with nitrogen to remove the oxygen and heated until 800°C and processed (activated) with heated water steam for 120 minutes.

The iodine number (%), is defined as the number of milligrams of iodine adsorbed from an agueous solution by 1 g of activated carbon when the iodine concentration of the residual filtrate is 0.02N. Granular activated carbon is pulverized (<0.1 mm) and then dried at 150°C to constant weight. Depending on the activity of the carbon, weigh 1g of the dried carbon, and transfer the weighed sample to a dry, glass stoppered 250 ml flask then add by pipette 50 ml of 0.10 N iodine solution. Stopper the flask immediately and shake it vigourously for 30 seconds. Filter by gravity through a filter paper immediately after the 30 seconds shaking period. Stir the filtrate in the breaker with a glass rod and pipette 50 ml into a 250 ml flask. Titrate the 50 ml sample with 0.10 N sodium thiosulphate solution until the yellow colour has almost disappeared. Add about 1 ml of starch solution and continue titration until the blue indicator

colour just disappears. Record the volume of sodium thiosulphate solution used.

To calculate the iodine number X of the carbon using the equation:

$$X\% = \frac{(V_0 - V_1) * 0.0127 * 100 * 50}{m * 10} \quad (1)$$

Where:

V_1 - *volume of sodium thiosulphate solution in ml,*

m - *mass of activated carbon in g,- iodine solution of 0.10 N added into weighed sample in ml,*

V_0 - *the volume of thiosulphate for blank test , ml*

0.0127 - *the atomic mass of iodine in 1ml 0.1 N thiosulphate solution*

The methylene blue adsorption value, mg/g is defined as the number of millilitres standart methylene blue solution decolourized by 0.1 g of activated carbon (dry basis). Granular activated carbon is pulverized (<0.1mm) and then dried at 150°C to constant weight. Contact exactly 0.1 g of the carbon sample with 25 ml of the methylene blue test solution in a glass stoppered flask. Shake until decolourization occurs. Then add a further 5 ml of the methylene blue test solution and shake until decolourization. Repeat the addition of methylene blue test solution in 5 ml portions as long as decolourization occurs within five minutes. Note the entire volume of test solution decolourized by the sample. Repeat the test to confirm the result obtained. The volume of methylene blue test solution in ml that is just decolourized, is the methylene blue value of the activated carbon.

The FTIR spectra of the samples were obtained on a Interspec 200-X series of FTIR spectrometers with PIKE Diffusion IR accessories using a KBr disc containing 1% finely ground samples. All the spectra were measured in the frequency range of 4000 to 400 1/cm, and 32 scans were taken per sample.

^{1}H-NMR and ^{13}C-NMR spectra were obtained with a BRUKER AVIII 600 MHz spectrometer. The sample (20 mg for 1H, 80 mg for 13C) were dissolved in deuterochloroform withchloroform as an internal standard. Chemical shifts are reported in ppm (δ).

RESULTS AND DISCUSSION

The results of ultimate, proximate and organic petrographic analysis of coal samples from Khoot deposit are shown in Table 1.

Results of proximate and ultimate analysis indicate that coal from Khoot deposit is a which is vitrinite-rich and has low ash and sulphur content. According to the ASTM D-388 classification it is of sub-bituminous coal. For the characterization of coal of Khoot deposit have been carried out IR analysis of coal samples (Figure 1).

In the IR spectra of Khoot (Figure 1) coals 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
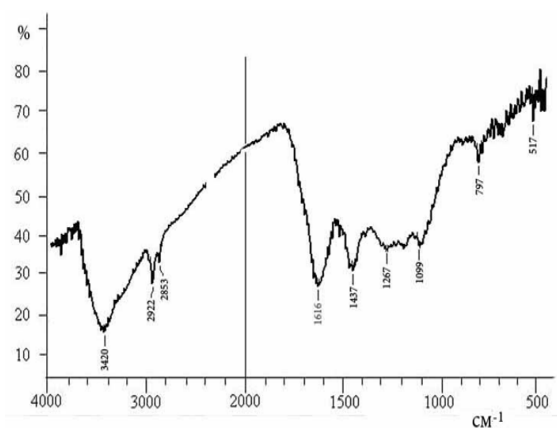

Fig. 1. The IR spectra of coal from Khoot deposit

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.

Petrographic analysis have been carried out on polished coal samples using the same microscope and software by point counting of 500 individual macerals. The white-black and colored petrographic photographs are presented in Figure 2 and the maceral group (vitrinite, inertinite and liptinite) composition is given in Table 2. The vitrinites are grey coloured fragments with different sizes and the inertinitesare white coloured stripes in white-black photograph (Figure 2 A).
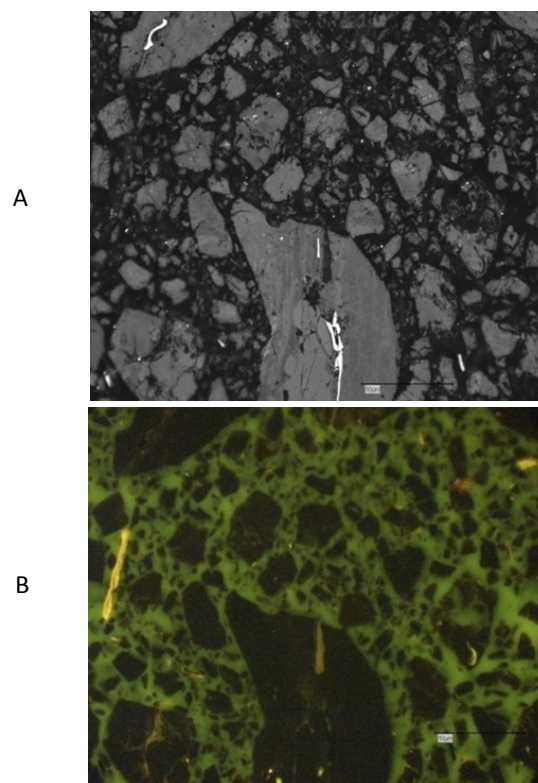

Fig. 2. The black-white (A) and coloured (B) petrographic photographs of polished coal sample of Khoot deposit.

Table 1. Proximate and Ultimate analyses of Khoot coal

Name of coal deposit	Moisture, W^a%	Ash, A^d,%	Yield of volatile matter, V^{daf} %	Sulphure S_t^d, %	Caloric value, Q^{daf} ксal/кg	Carbon, C^{daf}%	Hydrogen, H^{daf}%	N+O+ others, $(N+O)^{daf}$ %
Khoot	5.96	9.02	43.07	0.88	6004.00	73.11	5.39	21.50

$(N+O)^{daf}$ - bydifference; daf = dry, ash-free;

Table 2. Petrographic analysis results of Khoot coal.

№	Name of coal deposit	Vitrinite, %	Liptinite, %	Inertinite, %	Minerals, %
1	Khoot	88.00	4.00	5.00	3.00

But the liptinites are not observed in black-white photograph (Figure 2 A) and they are yellow coloured stripes in coloured photograph (Figure 2 B). The vitrinite's fragments are black coloured in coloured photograph (Figure 2 B). The polymeric (epoxide) binder is a black coloured background in black-white photograph (Figure 2 A) and a green coloured background in coloured photograph (Figure 2 B). The minerals in the polished coal sample are observed as a brilliant pieces in the microscope, but they are absent in black-white (A) and coloured (B) petrographic photographs.

pyrolysis. The yield of all liquid and gas products is 35.59% which is showing that there was an intensive thermolysis of the coal organic mass with higher degree of conversion.

As it is known that the organic mass of lignite and sub-bituminous coal characterizes with lower thermal stability and therefore they are more suitable for gasification and liquefaction [7].

Also the thermolysis experiments of Khoot coal in the medium tetralin (hydrogen donor solvent) have been carried out in a laboratory scale auvtoclav at 350 - 450°C and determined the yield of thermolysis

Table 3. The results of pyrolysis experiments of Khoot coal

Name of coal deposit	Temperature of pyrolysis,^{o}C	Hard residue, %	Tar, %	Pyrolytic water, %	Gas and loss, %
Khoot	550-600	64.16	9.93	13.6	12.31
		64.66	9.91	13.82	11.61
Averaged		64.41	9.92	13.71	11.96

The maceral group composition in Table 2 show that the organic matter of Khoot coal characterizes with highest content of vitrinite and lowest content of inertinite, liptinite and minerals connected with coal organic mass. The degree of vitrinite reflectance (RV^t=0.425%) was measured using an Axio Imager M2m microscope and Fossil software on 50 individual vitrinite macerals in random mode. This value 0.425% is characteristic for a sub-bituminous coal. Therefore the results of determined technical characteristics, elemental and maceral group composition, degree of vitrinite reflectance show that Khoot coal is a sub-bituminous coal which is suitable for thermal processing such as pyrolysis and thermolysis.

The Khoot coal was pyrolized in a bigger scale retort at 550 - 600°C and determined the yield of pyrolysis products including hard residue, tar, pyrolytic water and gas (Table 3).

The dates in Table 3 shown that 64.41% of organic mass of Khoot coal remained as a hard residue after

products including hard residue, tar and gas (Table 4). The dates in Table 4 show that the yield of hard residue is decreasing intensively and the yield of thermolysis products (tar and gas) are increasing intensively by the increasing of heating temperature. A highest yield (60.79%) of tar and gas obtained by using of mass ratio between coal and tetralin 1:1.8 at 450°C. At this condition 34.88% of organic mass of Khoot coal remained as a hard residue after thermolysis. The yield all liquid and gas products is 65.12% which is showing that there was also an intensive thermolysis of the coal organic mass with higher degree of conversion almost 2 times higher than that of pyrolysis.

The next step of our work is to investigate the obtained hard and liquid products after pyrolysis and thermolysis. The results of determined technical characteristics of initial coal sample, hard residues after pyrolysis and thermolysis are given in Table 5.

The dates in Table 5 show that the yield of volatile

Table 4. The results of thermolysis experiments of Khoot coal

Name of coal deposit	Donor-Solvent, g	Coal:solvent	Temperature, °C	Hard residue, %	Tar,%	Gas and loss,%
Khoot	Tetralin	1:1.8	350	79.49	19	1.51
			400	49.37	46.83	3.8
			450	34.88	60.79	4.33

matter of pyrolysis and thermolysis decreased 2.7 times in both case than that of initial coal sample. Also this is an indication for the intensive thermolysis of the coal organic mass.

One of the most important application of the hard residue after thermal processing is to produce activated carbon. For this reason the hard residue after pyrolysis was activated by preheated water steam at 800°C for 140 min, and determined the adsorption capacity of methylene blue and iodine of

Table 5. Characteristics of solid product of pyrolysis and thermolysis of Khoot coal

	Name of coal deposit	Moisture, W^a, %	Ash, % $A^{d,}$	Volatile matter, % V^{daf}
Khoot	Initial coal sample	5.96	9.02	43.07
	Hard residue after pyrolysis	0.27	11.58	16.70
	Hard residue after thermolysis (450⁰C)	2.44	22.47	17.72

the obtained activated carbon sample of Khoot coal (Table 6).

The dates in Table 6 show that the the ability of iodine adsorption of activated carbon is increased 4.1 times and that of methylene blue is same of the hard residue before activation. It means that mainly micro and meso pores have been formed during the pyrolysis and activation of Khoot coal.

To characterize the porosity structure of prepared activated carbon from pyrolysis hard residue in comparison with initial coal sample and thermolysis hard residue have used SEM analysis and the photographs are presented in Figure 3.

For the characterization of hard residue (C) after thermal dissolution have been carried out SEM analysis in comparison with that of initial coal sample (A), and it's activated carbon sample (B) and the photograph images are shown in Figure 3.

As it seen from the SEM images of A, B, C samples the form or behavior of initial coal sample, carbonized-activated carbon sample and hard residue after
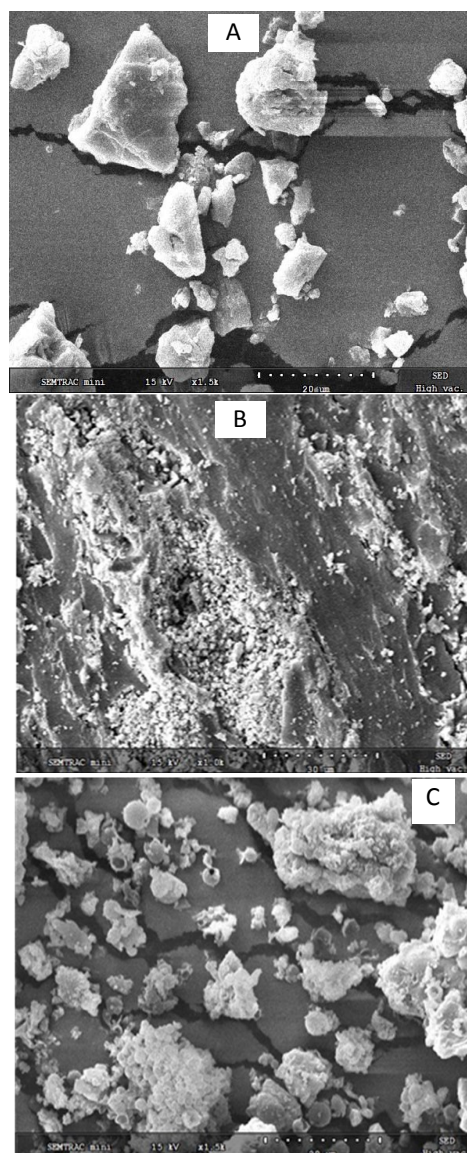

Fig. 3. SEM photographs: of Khoot coal (A), activated carbon of pyrolysis hard residue (B), thermolysis hard residue (C).

Table 6. The adsorption capacity of activated hard residue after pyrolysis

Name of coal deposit	Sample	Temperature, C°	Piece, mm	Time of activation, min	Metylene blue adsorption, mg/g	Iodine adsorption, %
Khoot	Hard residue after pyrolysis	0	1.5-0.63	0	0.2387	2.1
	Activated hard residue	800	1.5-0.63	140	0.2399	8.56

thermolysis are different. For example the SEM image of initial coal sample has a compact solid pieces. The SEM image of carbonized and activated carbon sample is a hard material with high developed porosity structure. The SEM image of hard residue after thermolysis in autoclave characterizes a hard pieces with micro porous structure in comparison with that of activated carbon sample.

For the characterization of liquid product after thermolysis have been carried out FT-IR, ^{13}C and ^{1}H NMR analysis and the spectrums are shown in Figure 4, - 6.

In the IR spectra of tar product after thermolysis in the presence of tetralin observed strong absorption bands for H of aromatic –CH group at 1590, 1480, 600 -700 cm^{-1} and for H of aliphatic –CH$_3$; –CH$_2$ and –CH groups at 2800-2920 and 1460 cm^{-1} and also for H of

-120 ppm; aliphatic C of –CH, –CH$_2$ and –CH$_3$ groups at 60-70 ppm. In the ^{1}H NMR spectra of liquid tar product after thermolysis in the presence of tetralin observed strong absorption bands for H of aromatic -CH group at 7 ppm and for H of aliphatic –CH$_3$; –CH$_2$ and –CH groups at 1-3 ppm. The ^{13}C and ^{1}HNMR spectra of liquid tar product show that the tar of Khoot coal after thermolysis also consists mainly aliphatic, aromatic and aromatic-aliphatic hydrocarbons.

Fig. 6. The ^{1}H NMR spectra of liquid tar product after thermolysis
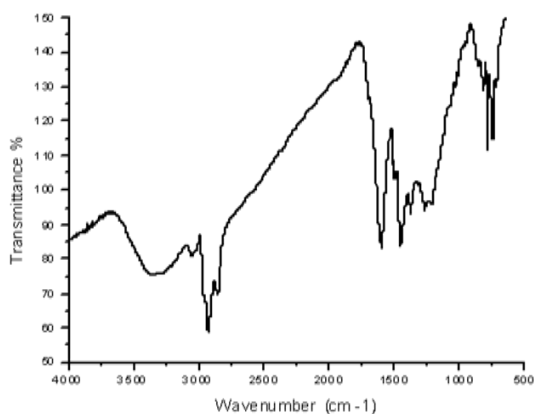

Fig. 4. The FT-IR spectra of liquid tar product after thermolysis.

–OH and –NH groups at 3400 - 3500 cm^{-1}. Therefore tar product of Khoot coal after thermolysis consists mainly aliphatic, aromatic and aromatic-aliphatic hydrocarbons. In the ^{13}C NMR spectra of liquid tar product after thermolysis observed aromatic C at 110
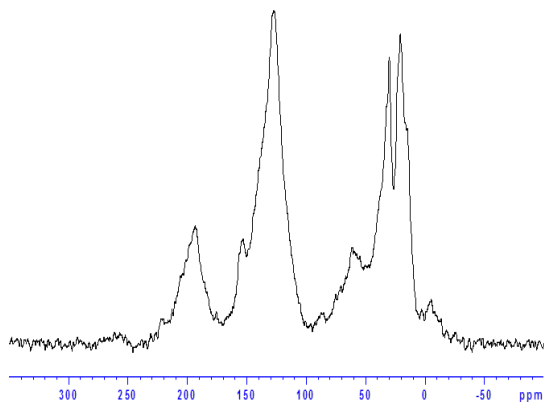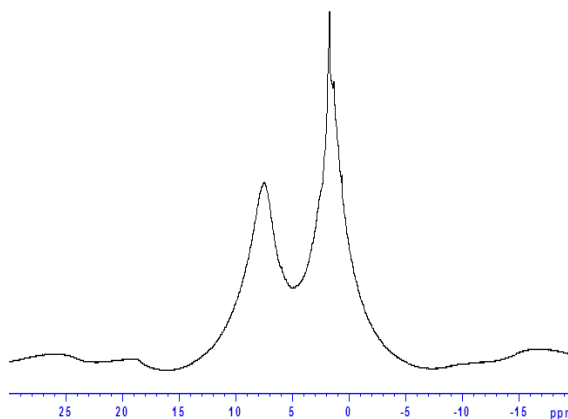

Fig. 5. The ^{13}C NMR spectra of liquid tar product after thermolysis.

CONCLUSIONS

1. On the basis of proximate, ultimate, petrographic and IR analysis have been confirmed that the Khoot coal is a subbituminous coal and it is suitable for thermal processing including pyrolysis and thermolysis.

2. The results of pyrolysis experiment of Khoot coal show that 64.41% of coal organic mass remained as a hard residue after pyrolysis. The yield of all liquid and gas products is 35.59% which is showing that there was an intensive thermolysis of the coal organic mass with higher degree of conversion.

3. The results of thermolysis of Khoot coal in tetralin with constant mass ratio between coal and tetralin (1:1.8) at 450°C show that 60.8% of liquid product can be obtained after thermolysis of the coal organic mass.

4. The ability of iodine adsorption of activated carbon is increased 4 times and that of methylene blue is same of the hard residue before activation. It means that mainly micro and meso pores have been formed during the pyrolysis and activation of Khoot coal.

5. The SEM image of initial coal sample has a compact solid pieces. The SEM image of carbonized and activated carbon sample is a hard material with high developed macro porosity structure. The SEM image of hard residue after thermolysis in autoclave characterizes a hard pieces with micro porous structure in comparison with that of activated carbon sample.

6. The IR, ^{13}C and ^{1}H NMR spectra of liquid tar

product show that the tar of Khoot coal after thermolysis also consists mainly aliphatic, aromatic and aromatic-aliphatic hydrocarbons.

REFERENCES

1. Medium-Term Coal Market Report 2013 - *Market Trends and Projections to 2018*, 144 pages, ISBN 978-92-64-19120-4.
2. Purevsuren B., Davaajav Ya., Erdenechimeg R. (2010) Investigation on largest coal deposits in Mongolia, Ed., Toonotprint, Ulaanbaatar (in Mongolian)
3. Purevsuren B. (2007) Coal is the main source of energy, In Abstracts of papers, *Second Korean and Mongolian Energy Conference,* Seoul: Yonsei Univ., 13.
4. Munkhjargal Sh. (1985) The benefication of the Tevshiingovi and Tavantolgoi coals. Dissertation, *Praha, UGG, CSW, (in Czech).*
5. Dugarjav J. (1995) Coking properties of Tavantolgoi coal. *Report of the Institute of chemistry, Mongolian Academy of Sciences, 17-22.*
6. Purevsuren B. *et al.* (2009) Thermal processing of Baganuur coal from Mongolia. *Annual Scientific Reports of ICCT, MAS,* **10**(36), 122-131.
7. Tsedevsuren Ts. *et al.* (1981) Hydrogenation of Bayanteeg coal of Mongolia, *Chemistry of Solid Fuels*, **6**, 17.
8. Avid B., Purevsuren B., Paterson N., Zhuo Y., *et al.* An exploratory investigation on the performance of Shivee-Ovoo coal and Khoot oil shale from Mongolia, Fuel, 83 (2004): 1105-1111.
9. Avid B., Purevsuren B. et al. (2004) Pyrolysis and TG analysis of the Shivee-Ovoo coal Mongolia. *Journal of Thermal Analysis and Calorimetry,* **68,** 877-885.
10. Ueda Sh. (1994) Preliminary survey on the Mongolian coal. *Annual Summary of Coal Liquefaction*, **19**, 140-150.
11. Taylor G.H., Teichmüller M., Davis A., Diessel C.F., *et al.* (1998), *Organic Petrology*, Gebr. Borntraeger Stuttgart, 704.