International Journal of Chemistry; Vol. 11, No. 2; 2019
ISSN 1916-9698 E-ISSN 1916-9701
Published by Canadian Center of Science and Education

Characterization of the Pyrolytic Products of Pine Nut Shells

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Received: April 22, 2019 Accepted: June 5, 2019 Online Published: June 20, 2019
doi:10.5539/ijc.v11n2p37 URL: https://doi.org/10.5539/ijc.v11n2p37

Abstract

Have been determined the technical characteristics and elemental composition of shells. The elemental composition of the shell was determined by a microanalytical method such as 5E C2000 model CNH-analyzer. The pyrolysis of shells investigated by using a standard quartz retort (tube) at different heating temperatures and determined the yields of pyrolysis products such as hard residue, tar, pyrolytic water, and gas. As a result of these experiments have been determined that 30% hard residue, higher yield 13% of tar, can be obtained at heating temperature 500°C. Thermogravimetric analysis of shells carried out in TG/DTA7200, Hitachi, Japan model equipment. The shells' ash chemical composition was first time determined by the X-ray diffractions powder, that it consists of significantly higher 40% these chemical elements including manganese, nickel, little zinc, sulfur, aluminum, phosphorus, iron, magnesium, and calcium. The solubility of purified pyrolysis tar of shells in hexane, benzene and dichloromethane were investigated by using silicagel column and the chemical composition of each fraction determined by using of GC/MS chromatography system. The FTIR spectra of shell and pyrolysis tar determined by using of a Nicolet 20-PC spectrometer. The porosity structure of activated pyrolysis hard residue determined by the SEM analysis.

Keywords: quartz retort, column chromatography, tar, activated carbon

1. Introduction

Mongolia is a rich country with different kinds natural organic raw materials including oil, coals, oil shale, wood and bioorganic materials of animal origin such as casein, animal bone and huge amounts of wastes of wood and plants origin and also plastics and so on (Purevsuren et al., 2017). The pine nuts grow in the forest area of Khangai and Khentii high mountains in Mongolia, which is a very limited area of 683900 hectares. Pine nuts (cedar) are edible seeds of pines. The pine nuts shell usually calls only ''shell''. The shell must be removed before the processing pine nuts. Therefore the shell is a solid waste material. Usually, people throw away the shell and pollute the environment. In 2016 Mongolia had exported about 466 kg of unshelled pine nuts and it means that about 1000 kg of a shell thrown away as wastes.

On the other hand, pyrolysis is an efficient method of treatment 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 (Davaajav & Purevsuren, 2006). As a result of pyrolysis can be obtained solid (hard residue), condensed liquid (tar and pyrolysis water) and gas (uncondensed) products (gases). The solid product is porous material with a higher caloric value which can be used as coke, semicoke, smokeless fuel, adsorbent material and so on. Tar is a petroleum-like product and can be used as a complex raw material for the production of chemical substances, gasoline, diesel, oils and so on (Ariunaa et al., 2007). The gas product can be used as gas fuel after cleaning of nitrogen and sulfur-containing pollutants in it (Batbileg et al., 2015; Davaajav & Purevsuren, 2006).

Before the pyrolysis experiments of organic raw materials have carried out a thermogravimetric analysis of these materials to determine the thermal stability characteristics such as thermostability indices ($T_{5\%}$, $T_{15\%}$ and $T_{25\%}$) and to evaluate how are easy for pyrolysis of them (Purevsuren, 1987). During the last decade, we are working on pyrolysis of some organic raw materials including different rank coals (Avid & Purevsuren, 2002; Munkhjargal & Purevsuren, 1998), oil shale (Avid, Purevsuren, & Dugarjav, 2000; Purevsuren & Ochirbat, 2016), wood waste (Otgonchuluun, Ariunaa, & Purevsuren, 2015), animal bone (Davaajav & Purevsuren, 2006; Purevsuren, Avid, Narangerel, Gerelmaa, & Davaajav, 2004), shell (Purevsuren, 2012), polypropylene waste (Purevsuren, Davaajav, Karaca, et al., 2009), milk casein

(Purevsuren & Davaajav, 2001b, 2001a), and characterization of obtained hard residue, tar and gas product after pyrolysis.

2. Experimental

Shells (as waste material) are a powdered and dried solid product with yellow-brown color. The shell was crushed into pieces of 3-6 mm size and the analytical sample was prepared by powdering to a particle size < 0.2 mm in a steel mill.

Analytical sample preparation (MNS 2719: 2001), proximate and ultimate analysis of shell 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 the shell was determined by a microanalytical method such as 5E C2000 model CNH-analyzer.

The FT-IR spectra of the shell were obtained on a Nicolet 20-PC FTIR spectrometer with CsI optics and DTGS detector. The KBr disc contained a 0.5% finely ground shell sample. All the spectra were measured in the frequency range of 4000 to 400 cm^{-1} and 32 scans were taken per sample.

Thermogravimetric analysis of shell carried out in TG/DTA 7200, Hitachi, Japan model equipment. Conditions of analysis were: Sample weight 5-10 mg. The heating temperature-range-20-1150^{o}C, heating rate- 40^{o}C/min, Carrier gas-in nitrogen, Crucible- made by Pt-Rh.

The small-scale pyrolysis experiments of shell samples were performed in a laboratory quartz retort (tube) which could contain air-dried and powdered to a particle size < 0.2 mm 1g. of shell sample. The retort was placed in a horizontal electric tube furnace with a maximum heating temperature of 950 ^{o}C. A chrome-alumni thermocouple was immersed in the tube furnace to measure the actual heating temperature. The pyrolysis experiments have been carried out at different heating temperatures 200-700 ^{o}C with a constant heating rate of 20 ^{o}C/min. First of all the quartz retort with the shell sample was heated for example to 600 ^{o}C with heating rate 20 ^{o}C/min. and kept at 700 ^{o}C for 80 min. The retort was connected with a thermostable glass tube heated also in a tube furnace at 80 ^{o}C for collecting of tars and this tube is also connected with an 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. The yields of pyrolysis products including solid residue (biochar), tar (condensed liquid product) and pyrolysis water determined by weighing, and the yield of gases by differences.

The preparative scale pyrolysis experiments of shell samples were performed in a laboratory vertical cylindrical retort made by stainless steel which could contain 1000g. of a sample. The retort was placed in an electric furnace (model SNOL) with a maximum temperature of 950 ^{o}C. A chrome-alumni thermocouple was immersed in the shell bed to measure the actual heating temperature and equipment for temperature control (potentiometer). The retort was connected with an air-cooled iron tube and water-cooled laboratory glass condenser and a collection vessel for the condensate of liquid product (tar 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^{o}C temperature and the heating rate was 20 ^{o}C min^{-1}. The yields of products including solid residue (biochar), tar and pyrolysis water determined by weighing, and the yield of gases by differences.

The liquid condensed by-product of shell pyrolysis consists from tar and pyrolysis water. They form an unmixed two layers and can be separated easily by separating the glass funnel. The upper layer is tar (viscous liquid) with a black-brown color and an unpleasant smell. The bottom layer is pyrolysis water (nonviscous liquid) with bad smell and yellow color. The final cleaning of tar from the pyrolysis water mixed with thermally treated $CaCl_2$ and separating (filtering or centrifuging). The yellow-colored pyrolysis water has a specific gravity-0.9227 g/cм^3 and solid residue-7.2% after evaporation in room temperature.

The pyrolyzed shell samples (10-15g.) were placed in quarts tube and flowed with nitrogen to remove the oxygen and heated until 800 ℃ and processed (activated) with heated water steam for 120 min.

The column chromatography conditions of pyrolysis tar of shell as follows:

- Small glass column: 5.0 mL
- Sample of tar 0.2g. for each solvent
- Used organic solvents (pure for chromatography): hexane, benzene and dichloromethane-20.0 mL from each solvent.
- Used sorbent: activated silica gel 4.0g.

The column chromatography carried out for obtaining the soluble in hexane (H), benzene (B) and dichloromethane (M) fractions of the pyrolysis tar. These fractions were used as a mother solution for GC/MS analysis. The organic solvent was evaporated from the obtained fraction for the determination of the yield of each fraction.

The conditions of the GC/MS analysis of each fraction are:

-The analytical sample of each fraction: 1 µml of each fraction in 1 mL of each solvent.

-The sample of GC/MS analysis: 1 µml from each analytical sample

-Used apparatus: Agilent 7890A Agilent 5975C GC-MS system and capillary column J W DB-5.30mx, 0.25mm I.D. 0.25 µm (122-5032).

-Carrier gas: He

-Mass range: 50-550.

- Starting temperature of the furnace: 100^{o}C.

-Heating temperature and time: 2200C, 46 min.

3. Results and Discussion

The proximate (basic technical characteristics) and ultimate (elemental composition) analysis of shells have been determined and the results are given in Table 1.

Table 1. Proximate and Ultimate analysis of shell

Proximate analysis, %					Ultimate analysis, %			
W^a	A^d	V^{daf}	Q^{daf} kcal/kg	S_{total}	C^{daf}	H^{daf}	N^{daf}	O^{daf}
9.97	0.69	75.90	4912.0	0.1	55.57	5.85	1.69	36.89

Dates in Table 1 show, there is a very little amount of ash in the shell, because it is a pure organic raw material. When it is heating, the organic mass is easy to decompose then makes a lot of volatile substances. The organic substances have low resistance for heat. The hydrogen and nitrogen content are in the average like in coals. The photograph pictures of pine nut shells (A) and it’s pyrolysis hard residue (B) are given in Figure 1.

A B

Figure 1. The photograph pictures of the shell (A) and it’s pyrolysis hard residue (B)

As it is known the shell is a solid material thrown away after removing the Pine nuts (are the edible seeds) with brown color and therefore it is a waste material. To use this waste material we have used pyrolysis as a useful method for processing of the shell. After pyrolysis, the shell became a solid material (hard residue or biochar) with a black color.

The analytical sample of the shell was a subject for FTIR analysis and the results are shown in Figure 2.

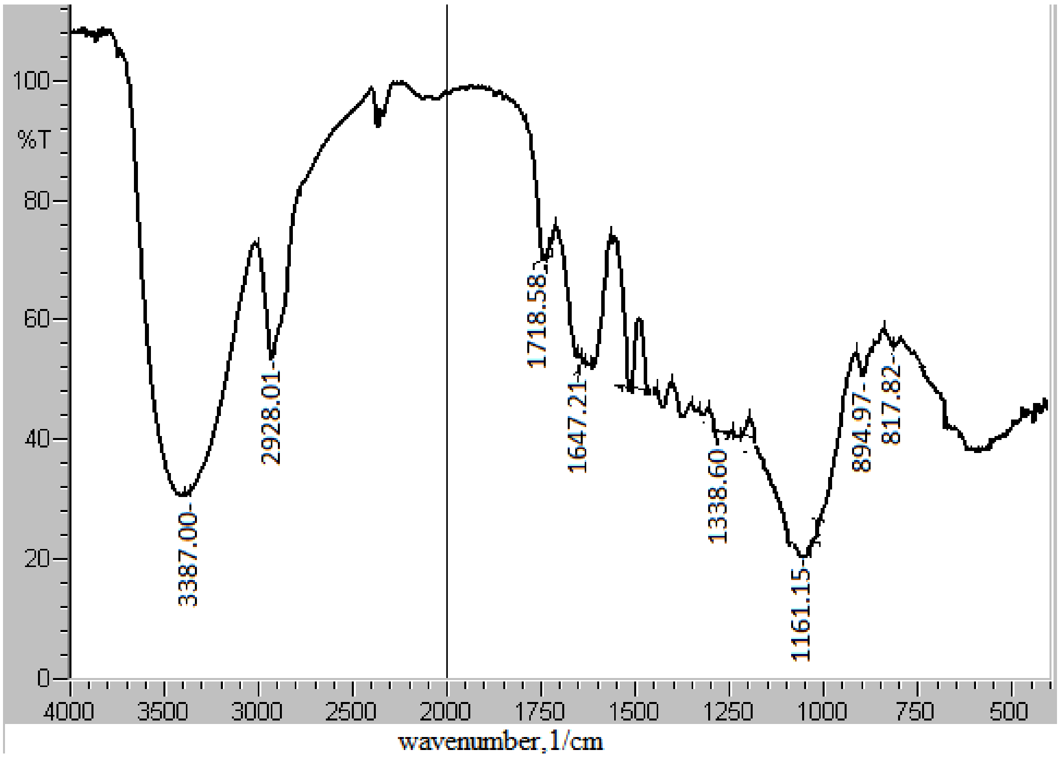


Figure 2. The FTIR spectra of shell

Figure 2 shows, in the FTIR spectra of shell has a very intensive unsharp pick at 3387 cm^{-1} for hydrogen from –OH, >NH, and –NH_2 groups, a strong absorption band exists at 2926 cm^{-1} for aliphatic >CH_2, -CH_3 and >CH- groups. A week band at 1718-1739 cm^{-1} for –COOH and a strong unsharp pick at 1652-1624cm^{-1} for >CO groups. There are very little bands at 1608 cm^{-1}, 1338 cm^{-1}, 1319cm^{-1}, 1271cm^{-1}, 1228cm^{-1} for –C-O- groups, at 1161cm^{-1}, 1109cm^{-1}, 1055cm^{-1}, 1033cm^{-1} for aromatic –OH groups and at 700-900 cm^{-1} for aromatic -C=C- groups (Monkhoobor & Batchimeg, 2009).

We have been collected the ash of shell during analysis and pyrolysis experiments and burned completely for analysis of the inorganic matters in a shell. The chemical composition of ash from the shell determined the first time by the X-ray diffractions powder and see from results, the content of K_2O (48.3%) is highest and the content of MgO (15.3%), CaO (10.8%) is also higher. It was very interesting that the ash of shell has also some amounts of Al_2O_3, SiO_2, P_2O_5, SO_3, Fe_2O_3, Mn_2O_3 and ZnO (4.2%, 6.4%, 6.4%, 3.7%, 2.0%,1.3%, and 1.1%). The lowest content has only CuO and NiO. Also, have been determined the value of the ratio between sum oxides (Fe_2O_3+ CaO + MgO +Na_2 O + K_2 O)/(SiO_2 +Al_2O_3+ TiO_2) =7.19 which is more than one (>1.0) and this value is an indication that the ash of shell has a basic character. Also, the ash of shell was a subject for X-ray diffractions powder analysis and the results are given in Figure 3.

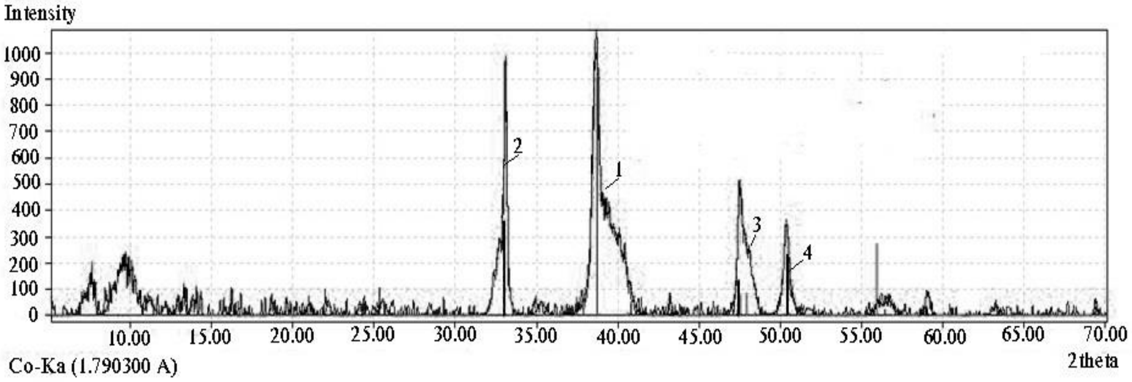


Figure 3. The X-ray diffractions powder of shell

As a result of X-ray diffractions powder of shell ash have been determined that the shell ash consists mostly following minerals:

1-calcium aluminum oxide ($Ca_3 AI_2 O_6$) 66.61 %

2-Potassium Chloride (KCI) 26.49%

3-Magnesium oxide (MgO) 5.70 %

4- Manganese oxide (MnO) 1.20 %

The analytical shell sample was investigated by thermogravimetric analysis and results are shown in Figure 4.

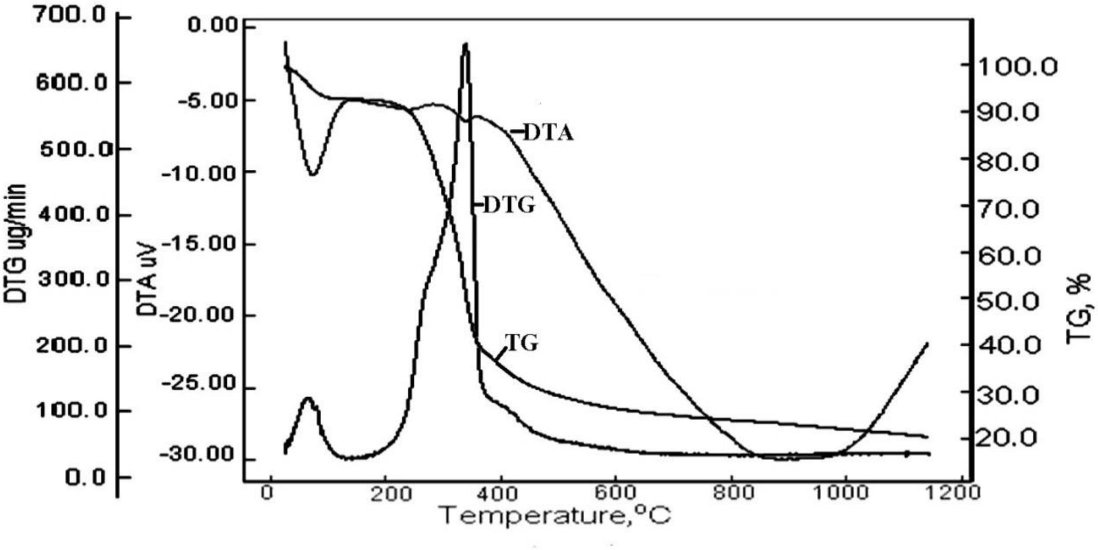


Figure 4. Thermogravimetric curves of shell

Heating of shell sample at 25-1100 ^{o}C temperatures in nitrogen atmosphere show that the thermal decomposition of shell ended with about 20% weight loss and 80% hard residue at 1100 ^{o}C (Figure 3). The TG curve in Figure 4 consists of different temperature intervals (steps) such as 30 -170^{o}C; 170-395^{o}C; 395-700^{o}C; 700-1100^{o}C. In the first step (30-170 ^{0}C) the weight loss belongs to releasing some absorbed gas and moisture from the shell sample. In the second step (300-600^{o}C) starts intensively thermal decomposition of the organic matter of shell sample and forming a liquid (tar and pyrolysis water) and gas products during the pyrolysis. In the third (600 -800^{o}C) and fourth (800-1100^{o}C) steps the weight loss is decreasing intensively, which is an indication for finishing thermal decomposition and starting carbonization of shell sample. On the basis of TG curve (Weight loss,% vs Heating temperatures, ^{o}C in Figure 4) have been measured the thermal stability indices $T_{5\%}$,$T_{15\%}$, $T_{25\%}$ of the shell during it's thermal degradation in nitrogen atmosphere (Table 2). These indices are the temperatures in which the weight loss are 5%, 15% and 25%.

Table 2. The thermal stability indices ($T_{5\%}$,$T_{15\%}$, and $T_{25\%}$) of shell

Sample	Thermal stability indices, ^{o}C		
	T_5%	T_{15}%	T_{25}%
Shell	72.49	266.27	295.39

The values or these indices are comparatively lower and it means that the shell has lower thermal stability during its heating or pyrolysis.

Pyrolysis is one of an important process of utilization of organic raw materials including organic wastes for the production of solid, liquid and gas products. The pyrolysis experiments of shells carried out in a nitrogen atmosphere at different heating temperatures and determined the yields of obtained solid, condensed liquid and uncondensed gas products (Figure 5).

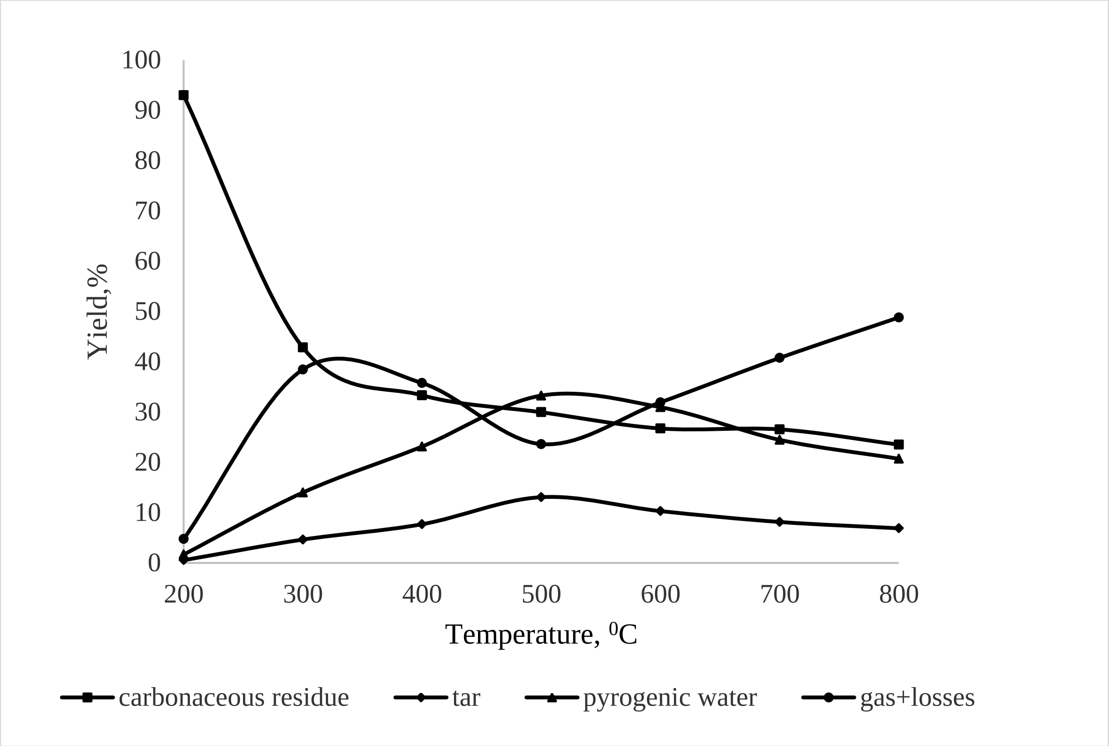


Figure 5. The yields of pyrolysis products of shell at different heating temperatures

Pyrolysis of the shell was performed in a standard laboratory quartz retort at different heating temperatures with constant heating rate-20℃/min and the yields of products include

ing biochar, tar, pyrolysis water determined by weighing and the yield of uncondensed gas by differences (Figure 5).

These results show that the yield of tar, pyrolysis water and gas increased with raising the temperature of pyrolysis. Only the yield of hard residue was decreased at the same time. The formed tar and hard residue were the most important products for us. Certainly, the yield of tar is lower at lower temperatures, because the thermal decomposition was not enough. The optimum temperature for pyrolysis of the shell was selected 500^{0}C, in which the yield of tar is higher-13.09%.

The yields of pyrolysis products of shell obtained in this condition compared with the yields of other organic materials investigated by us are given in Table 3.

Table 3. The yields of pyrolysis products of shell and other organic materials

№	Name of materials	Hard residue, %	Pyrolysis water, %	Gas,%	Tar, %
1	Shell	29.98	33.29	23.64	13.09
2	Casein	28.33	13.23	20.84	37.38
3	Animal bone	70.00	7.60	17.47	4.92
4	Oil shale	73.45	3.93	6.99	15.62
5	Brown coal	68.31	7.14	15.54	8.71
6	Wood waste	27.20	20.04	31.30	21.46

Shell as a pure organic material like casein and wood has the lowest ash content and highest organic matter, therefore shell gives the lowest yield of hard residue and the higher yield of pyrolysis liquid (tar and pyrolysis water) and gas products (Table 3). In the case of animal bone, the yields of hard residue and pyrolysis liquid products are similar or same as for oil shale and brown coal (Table 3), because of its higher mineral matter and lower organic matter content (Purevsuren, Davaajav, F, et al., 2009).

Usually, the solid product can be used as a carbonaceous material, smokeless fuel, activated carbon and liquid product as a complex raw material for the production of chemical substances. Gas products can be used as gas fuel after cleaning of N and S containing gases. For this reason, we have been characterized by the solid and liquid products of the pyrolysis of the shell. First of all, have been determined the technical characteristics of the hard residue (solid product) after pyrolysis of the shell. The proximate analysis results, the volatile matter content decreased 10 times (V^{daf} 7.54%, W^{a} -0.83%, A^{d} 2.07and Q^{daf} -7320.62 kcal/kg) and much more increased caloric value in comparison with the initial shell characteristics in Table1, which are an indication for intensive thermal decomposition of the organic mass of the shell. Due to the carbonization process of its organic mass, there is slightly increasing the ash content.

To prepare an activated carbon-based on pyrolysis hard residue of the shell has been used an activation process at $800^{o}C$ with preheated water steam for 80 min. and obtained black colored carbonized solid material with high developed porosity structures visually. For evaluation, the adsorption capacity of the activated carbon and hard residue have been determined the adsorption value of methylene blue and iodine and the results are given in Table 4.

Table 4.The adsorption capacity of activated hard residue after pyrolysis

№	Sample	Adsorption of methylene blue, mg/g	Iodine number, %
1	Hard residue after pyrolysis	14.4	1.20
2	Activated hard residue	358.0	54.3

The results in Table 4 show that the methylene blue adsorption valued strongly increased 25 times and iodine adsorption 45 times than that of pyrolysis hard residue, which are an indication for a good activated carbon with high developed porosity structures.

For the visual evaluation of the porosity structure of the activated carbon of shell have used SEM analysis and photographic pictures with different sizes are given in Figure 6.

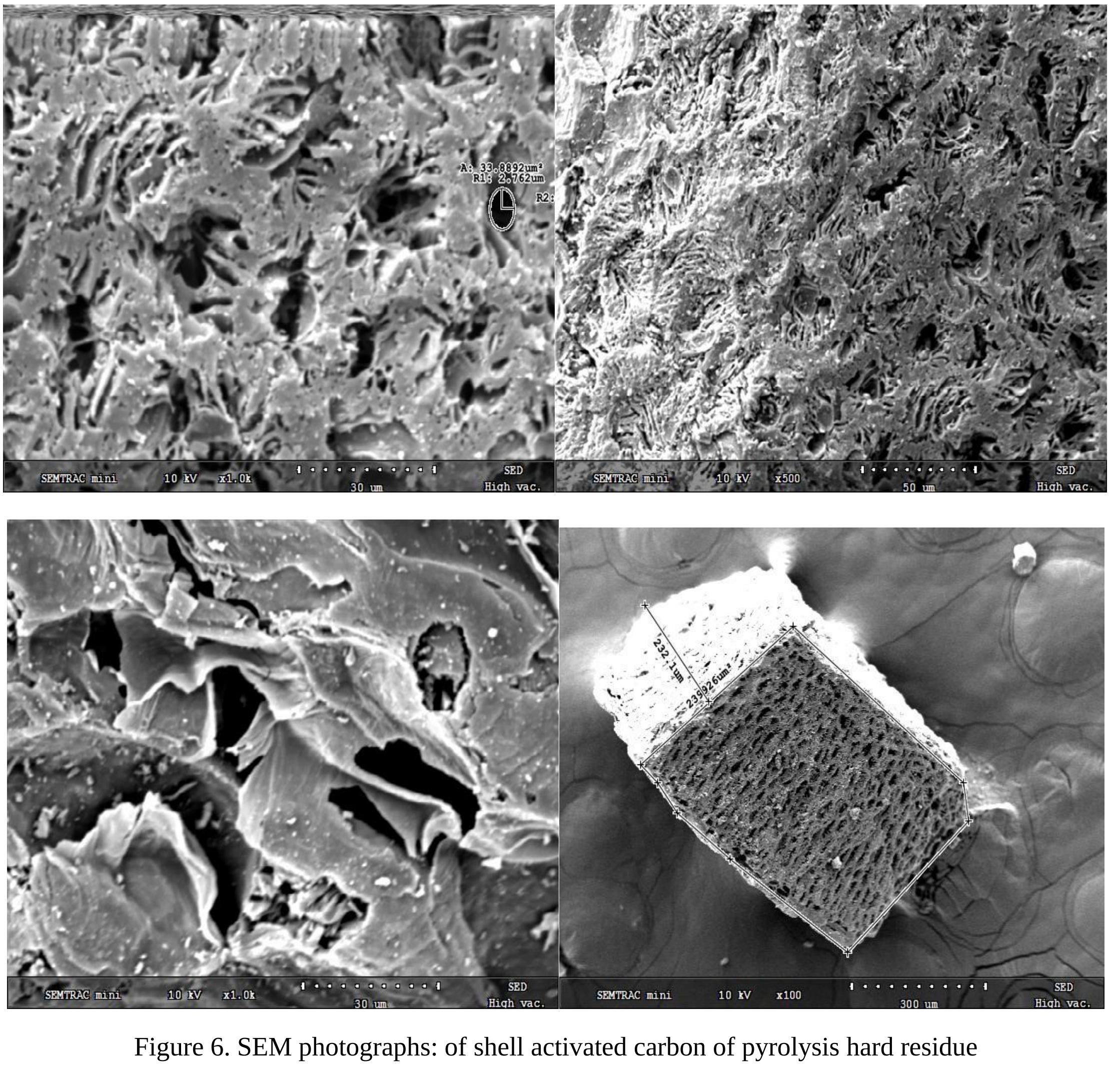


Figure 6. SEM photographs: of shell activated carbon of pyrolysis hard residue

There are huge spread smoothly of waste shell pyrolysis solid residues. The SEM image different sizes activated carbon sample is high developed micro and mesoporous structure. The chemical analysis of methylene blue and iodine (Table 4) and SEM analysis results show that an activated carbon with good adsorption ability and high developed porosity structures can be prepared on the bases of pyrolysis hard residue of the shell.

As mentioned above the condensed liquid tar is one of the most important products of the pyrolysis. For this reason, we have been carried out more detailed investigations on characterization by spectrometric and chromatographic analysis. For example the FTIR spectra of pyrolysis tar of shell shown in Figure 7.

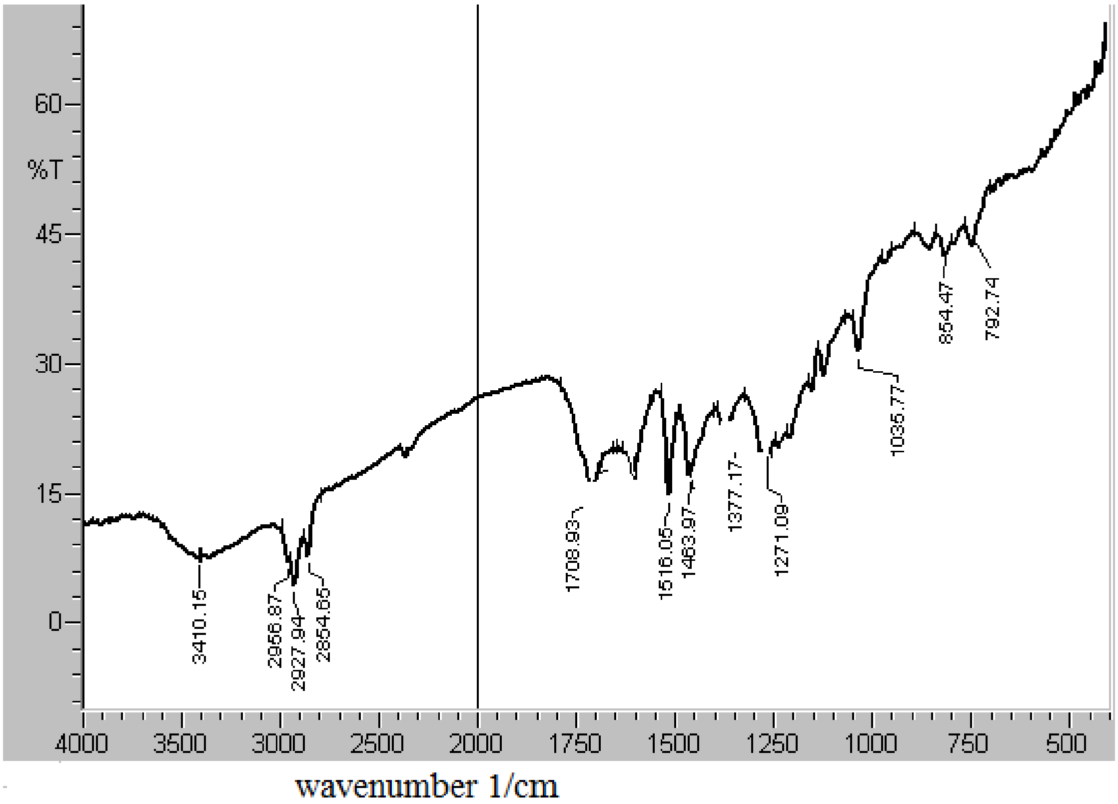


Figure 7. The FTIR spectra of pyrolysis tar of shell

There are in the FTIR spectra of pyrolysis tar of shell have poor picks of aromatic -C=C- groups at 702-968 cm^{-1}, picks with less intensity for aromatic –OH groups at 1035-1153 cm^{-1} and for –C-O- groups at 1207-1377 cm^{-1}, picks with more intensity for >CO groups at 1458-1516 cm^{-1} and for aliphatic >CH$_2$, -CH$_3$ and >CH- groups at 2854-2958 cm^{-1}, less intensive unsharp wide pick at 3410 and for –COOH groups at 1653-1708 and also for >CO groups at 1608 cm^{-1}. The IR spectra of pyrolysis tar of shell show that the tar is multifunctional complex organic material with bad smelts and black-brown color (Monkhoobor & Batchimeg, 2009).

As shown as, the chemical composition in group organic compounds of pyrolysis tar of shell that most part of the tar consists of neutral oils 89.5%, the content of free carbons 5.4%, phenols and asphaltenes are content 1.7% and 2.6%, and less organic bases and acids than others (0.1% and 0.7%).

Also, the pyrolysis tar of shell was distilled at room temperature and obtained 4 fractions with different boiling temperature range and the yields of fractions are given in Table 5.

Table 5. The yield of distillation fractions of pyrolysis tar of shell with different boiling temperatures

Boiling temperature range, ℃	Yield of fractions, %	n	Appearance
From the beginning of boiling to 180 ℃ хүртэл	10.30	1.475	Light fraction with white-yellow color
180-250 ℃	32.99	1.512	Middle fraction with brown color
250-280 ℃	21.32	1.519	Middle fraction with black-brown color
280<	35.39	-	Heavy fraction (distillation residue) with black color

The data in Table 5 shows that two middle fractions have the highest content and a heavy fraction has higher content, only the light fraction has the lowest content.

The pyrolysis tar of shell was a subject of silica gel chromatography separation and hexane, benzene and dichloromethane are used as eluents. The yields of obtained fractions of soluble in hexane, benzene, and dichloromethane are given in Table 6 and determined the chemical compositions of each fraction by GC/MS chromatography are shown in Figure 8,9 and 10.

Table 6. The yields of fractions of tar by silicagel chromatography, %

Hexan soluble fraction (H)	Benzene soluble fraction (B)	Dichloromethane soluble fraction (M)	All separated fractions
1.58	18.91	14.59	35.08

The results of silica gel chromatography of shell tar show that most part of tar is soluble in benzene and less part of tar is soluble in hexane, which means that most parts of tar consist aromatic hydrocarbons.

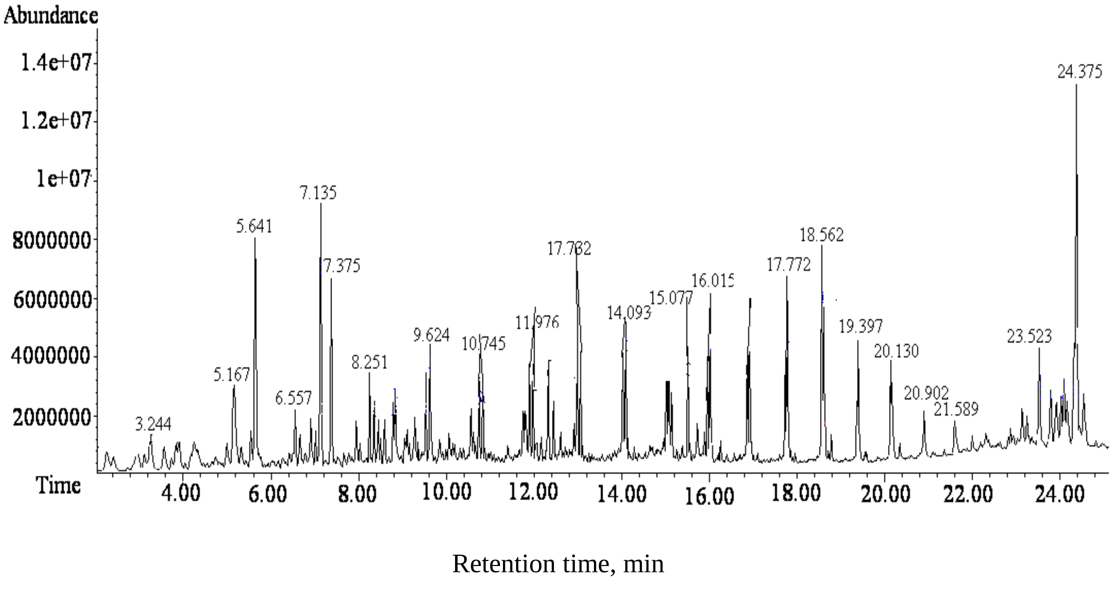
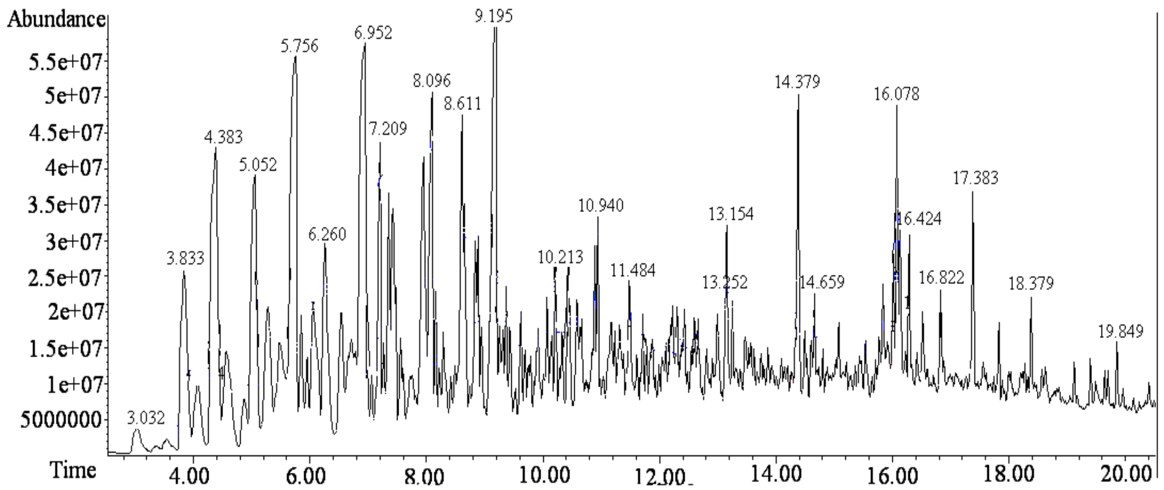
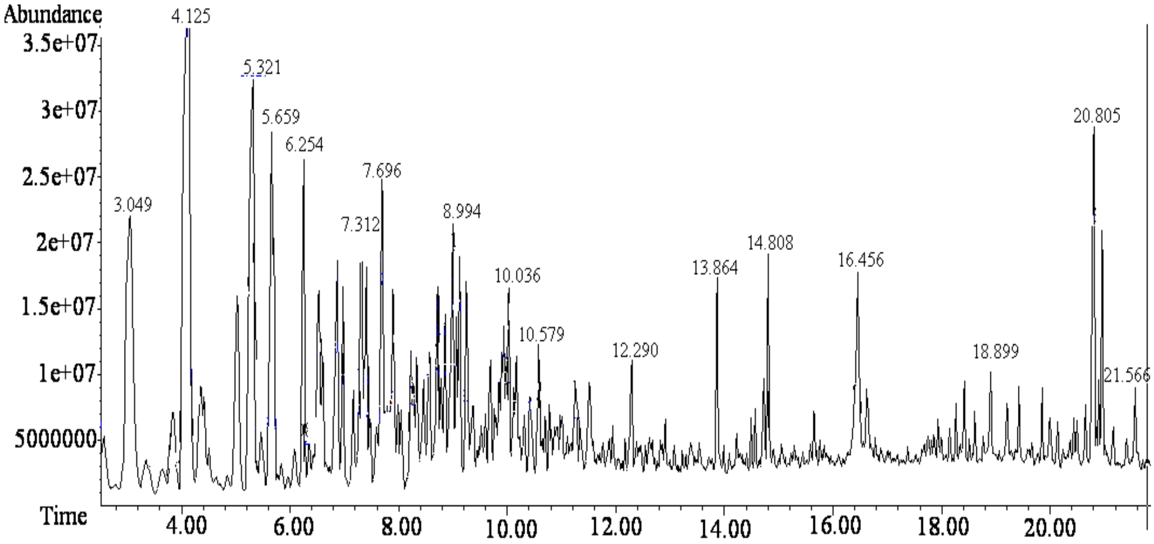


Figure 8. GC/MS chromatogram of hexane soluble fraction



Retention time, min

Figure 9. GC/MS chromatogram of benzene soluble fraction



Retention time, min

Figure 10. GC/MS chromatogram of dichlorometane soluble fraction

All registered and identified peaks of GC/MS analysis for pyrolysis tar of shell soluble in hexane, benzene, and dichloromethane fractions are given in Table 7 and the names of all identified peaks are in appendix-1.

Table 7. All registered and identified peaks of GC/MS chromatograms of each fractions

GC/MS compositions of tar	Hexane soluble fraction (H), %		Benzene soluble fraction (B) %		Dichloromethane soluble fraction (M) %	
	All registered peaks	All identified peaks	All registered peaks	All identified peaks	All registered peaks	All identified peaks
GC/MS chromatograms peak	55	48	91	39	65	29

As a results of GC/MS analysis for pyrolysis tar of shell soluble in hexane, benzene and dichloromethane fractions determined and identified 48 (from all registered 55 hexane soluble compounds), 39 (from all registered 91 benzene soluble compounds) and 29 (from all registered 65 dichloromethane soluble compounds) organic compounds (appendix-1). In general, pyrolysis tars organic raw materials to be extremely complex mixtures. Pioneering GCMS analyses have shown that biomass pyrolysis tars contain very large numbers of chemical components, significant proportions of which are oxygenated compounds (Morgan & Kandiyoti, 2014).

4. Conclusions

1. On the basis of proximate, ultimate, and FTIR analysis, it can be concluded that the shell is an organic raw material which is suitable for pyrolysis. The shell’s ash contains high potassium.
2. The results of the pyrolysis experiment of shell show that 29.98% of shell organic mass remained as a hard residue after pyrolysis. The yield of liquid and gas products is 70.02% which shows that there was an intensive thermal decomposition of the shell organic mass with a higher degree of conversion.
3. As a results of GC/MS analysis of tar of shell soluble in hexane, benzene and dichloromethane fractions determined and identified 48 (from all registered 55 hexane soluble compounds), 39 (from all registered 91 benzene soluble compounds) and 29 (from all registered 65 dichloromethane soluble compounds) organic compounds. These are consist of carbons like aromatic and alkyl-aromatic, long-chain aliphatic.
4. Therefore, the FTIR spectra and GC/MS analysis of pyrolysis tar of shell show that the tar is multifunctional complex organic material with bad smelts and black-brown color.
5. The prepared activated carbon of pyrolysis hard residue of shell and the pyrolysis hard residue of shell were tested for methylene blue and iodine adsorption and the results show that the methylene blue adsorption strongly increased 25 times and iodine adsorption 45 times increased than that of pyrolysis hard residue, which are an indication for a good activated carbon.
6. On the basis of thermogravimetric analysis of shell have been determined following thermal stability indices such as $T_{5\%}$ =72.49 ^{o}C; $T_{15\%}$ = 266.27 ^{o}C; $T_{25\%}$ = 295.39 ^{o}C. These thermal stability indices show that shell has lower thermal stability and a bid exothermic reaction peak at 300 ^{0}C related to intensive thermal destruction of the coal organic mass of the sample.
7. The proximate analysis results of hard residue after pyrolysis of shell show that the volatile matter content decreased 10 times and much more increased caloric value in comparison with the initial shell characteristics, which are an indication for intensive thermal decomposition of the organic mass of the shell. Due to the carbonization process of its organic mass, there is slightly increasing the ash content.

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Appendix-1.The name of determined organic substances by GC/MS chromatography

Soluble in Hexane fraction			Soluble in Benzene fraction			Soluble in Dichloromethane fraction		
R.T	% of	The name of determined organic	R.T	% of	The name of determined organic	R.T	% of	The name of determined
1.527	23.240	Hexan	1.585	3.182	Benzene	1.642	7.309	Benzene
2.254	0.796	Dimethyl benzene	3.833	3.754	2-methyl, phenol	2.569	1.202	1-(2-furanyl) ethanone,
2.935	0.744	Methyl ethyl benzene	4.074	1.212	4-methyl , phenol	3.049	7.122	Phenol
3.244	1.195	Benzene cyclopropyl	4.383	6.494	4-methoxy, phenol	3.833	1.508	2-methyl phenol
3.559	0.724	Diethyl benzene	4.566	2.302	2, 4-dimethyl, phenol	4.125	12.318	3-methyl phenol
5.167	2.864	Benzene (cyclopopenyl 1-methyl)	4.875	0.771	2-ethyl, phenol	4.354	1.318	2-methoxy phenol
5.641	4.448	Naphthalene	5.275	2.066	2, 3-dimethyl, phenol	5.023	3.072	dimethyl phenol
6.557	1.102	1,3-dimethyl, 1H-indene	5.756	6.899	2-methoxy 4-methyl, phenol	5.321	7.374	dimethyl phenol
6.912	0.845	1-Tridecene	6.059	2.218	4,7- dimethyl Benzofuran	5.470	0.700	dimethyl phenol
7.135	4.136	1-methyl naphthalene	6.260	2.991	2-ethyl 6-methyl, phenol	5.659	3.832	dimethyl phenol
7.375	2.720	2-methyl naphthalene	6.540	1.610	2- (2 methylpropyl) phenol	6.254	2.890	2,3-dimethyl toluene
8.258	1.033	2-Tetradecene	6.952	5.985	Methoxy ethylphenol	6.528	2.072	3-ethyl 5-methyl phenol
8.594	0.726	2,7- dimethyl, naphthalene	7.209	2.614	1-methyl Naphthalene,	6.866	2.359	4-ethyl 2-methoxy phenol
8.794	0.833	2,3- dimethyl, naphthalene	7.352	1.344	2-methoxy 4-vinylphenol	6.975	1.443	2,3-dihydro 1H inden
8.840	0.973	1,7- dimethyl, naphthalene	7.947	3.276	2-methoxy 3- (2-propenyl) phenol	7.163	0.708	2-methyl naphthalene
9.286	0.837	Benzene, octyl	8.096	3.177	3-ethoxy 4-gidroxy Benzaldehyde	7.312	2.173	2-ethyl 3-methoxy pyrazine
9.532	0.914	1-Pentadecene	8.291	0.659	Biphenyl	7.404	1.059	4-ethyl 1,2-dimethoxy
9.624	1.560	Pentadecene	8.611	1.657	2-methoxy-4-(1-propenyl) phenol	7.696	2.212	6-methoxy o-cresol
10.562	0.698	Benzene, nonyl	8.834	1.205	1,7-dimeyhyl naphthalene	7.896	1.267	1H-indenol
10.745	1.047	1-Hexadecene	8.886	0.830	2,6-dimeyhyl naphthalene	8.714	1.336	2-methyl 5
10.831	0.961	Hexadecene	9.195	6.230	2-methoxy-4-(1-propenyl) phenol	8.994	2.131	3,4-methylenedioxyamisole
11.747	0.908	Benzene, decyl	10.213	0.791	1,6,7-trimeyhyl naphthalene	9.126	1.578	2-methoxy- 4-(1-propenyl)
11.804	0.858	8-Heptadecene	10.425	0.862	1,4,6-trimeyhyl naphthalene	9.246	1.644	5,7-dimethyl 1H-indazole
11.896	0.983	1- Heptadecene	10.213	0.791	Naphthalene, 1,6,7-trimeyhyl	10.036	0.865	2- naphthalenol
11.976	1.325	Heptadecene	10.425	0.862	Naphthalene, 1,4,6-trimeyhyl	13.864	1.160	1,2-benzenedicarboxylic
12.325	1.189	1,2-isohexyl 6-methyl, 1-heptene	10.889	0.556	9 H fluorene	14.808	1.182	dibutyl phathalate
12.445	0.733	1,2,3-trimethyl, cyclohexane	10.940	0.787	1,4,5-trimeyhyl naphthalene	16.456	1.938	9-Octadecenoic acid
12.988	1.343	1-Octadecene	11.169	0.905	2-methyl 1-naphthalenol	20.805	2.813	Tribenzo(a,c,e) cycloocten
13.063	1.069	Octadecene	12.657	0.483	1,2-dimethyl naphtho (2,1-6)	20.959	1.199	2-(3,4-dimethoxy phenyl)
14.030	1.378	1-Nonadecene	13.154	1.326	Phenanthrene			
14.063	1.467	Nonadecane	14.379	1.731	Hexadecanoic acid, methyl ester			
15.020	1.429	1- Octadecene	15.838	0.433	di-p-Tolylacetylene			
15.077	1.525	Eicosane	16.015	0.547	9,12-octadecadienoic acid,			
15.140	0.839	Dimethyl, phenanthrene	16.078	1.448%	9- octadecanoic acid, methyl			
15.512	1.317	Dimethyl isopropyl	16.124	0.890%	9- octadecanoic acid, methyl			
15.958	1.078	10-Heneicosene	16.284	0.672%	9- octadecanoic acid, methyl			
16.015	1.586	Heneicosene	16.822	0.552%	2,3,5-trimethyl phenanthrene			
16.862	1.116	1-Docosene	17.383	1.037%	1-methyl-7-(1-methylethyl)			
16.914	1.400	Docosane	18.379	0.402%	1-Phenanthrenecarboxyhi acid,			
17.732	1.087	9-Tricosene	21.142	0.284%	Tetracosanoic acid, methyl ester			
17.772	2.209	Tricosane						
18.562	2.373	Cyclotetracosane						
18.602	1.108	Tetracosane						
19.397	1.556	Pentacosane						
20.130	1.109	1-Hexacosene						
20.902	0.968	Heptacosane						
23.786	0.984	2-Anthracenecarboxylic acid,						
24.375	5.907	3,5-diene Stigmastan						