The Dependence of Humic Acids Content of the Oltenia Lignite, Function of the Macropetrographic Constituents (Litotypes)

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Abstract

Wood brown coal (lignite) from the Pliocene Oltenia (photo 1) were divided into three constituent's macropetrographics, litotypes, and analyzed in order to identify the differences in behavior that occur depending on the technology layer exploited. There was chosen to analyze the humic acids extracted from lignite, being the main carriers of property by briquetting without binder and the characteristics of fertilizers in plant nutrition and soil improvement. There were detected significant differences linked to the chemical age (level of in carbonization) as well as the petrographic structure of the coal layer exploited.

Keywords: lignite, humic acids, litotypes

Introduction

Over 80% of fossil fuel reserves of Romania consist of Pliocene lignite deposits in the area of Sub-Carpathian Oltenia (photo 1). Coal deposits strongly tectonized with multiple layers of various thickness and different macroscopic components (litotypes) and microscopic (macerated and micro litotypes), different hydro - geological conditions and mineral components of a differentiated epigenetic and syngenetic origin have been exploited. In order to obtain an uniform production of lignite and according to actual norms and standards the resulted product from all the machines of extraction is been mixed and it resulted an average function of the layer, time, geographic or administrative zone and even on carbonifer region. The destination of this inferior coal was initially that of energetic fuel (for burning in high capacity thermopower stations) or as domestic fuel. From this current standard production [7] there have been collected medium samples considered to be representative out of which there have been made different researches in order to enrich the fuel mass of this inferior coal as well as its valorification in using the xiloidic component or its content in humic acids, humines and extractable humates [2,3,4,5,6].

Fundamental studies, which are the base of the classification of certain coals, have also been made out of these medium samples which are in accordance with the actual standards and technical sheets of the product [7] but the geological and citologycal characterization of these coal layers show major differences between coal beds which are exploited (between 5 and 20 exploitable beds[6,7] due to the petrographical structure as well as the microscopic constituents of the lignite in each bed [6]. The specialists specify that the principal litotypes of the pliocenic lignite from Oltenia are [6]:

1. The detritic coal represents over 50% from total volume of the lignite as independent beds.
2. The xilitic coal is the intermediary litotype, the most important; it representing over 30% of the exploited lignites. Their properties are function the xilit and detritic coal ratio, the xilit content being over 20%, and reaches in some beds over 80% (V–VII beds).
3. The low xilitic coal- is a litotype made from of an alternance of stripes of detritic coal and thin ones (milimetric) of less than 10% xilit.

Although these details made by geologists are known in the technical description [7] for all coal depots from Oltenia, the content in xilit is between 3.8-7.88%. Although this discrepancy doesn't affect the use of the lignite as fuel except the grinding operation of the coal in order to be burned by pulverization, for other uses the quantity of the litotypes affects the final product and especially the specific consumptions.

This deep applicative study was initiated as result of the researches in the pilot phase of using the lignite in order to obtain a cheap active coal for epuration of wastewaters and to obtain organo-mineral fertilizer with high content of humic acids and aiming to explain some differences between technological research during the pilot phase and the research during the laboratory phase.

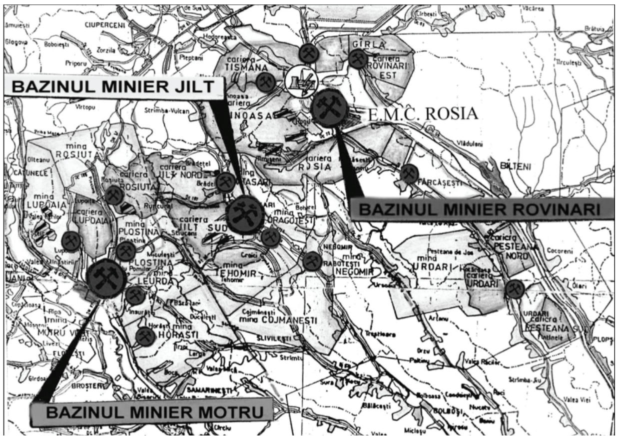

Photo 1. The coal depots Oltenia – Romania

Foto. 1. Złoże węgla Oltenia w Rumunii

Tab. 1. Elementary composition of carbo-generators (%)

Tab. 1.Analiza elementarna składników węglotwórczych (%)

Carbo-generators	C	H	O	N	S
Cellulose	44.4	6.2	49.4	–	–
Lignine	63.1	5.9	31.0	–	–
Albumines	50–55	6.5–7.2	20–23	15–19	0.3–2.4
Fats	70–79	11–13	10–12	–	–
Waxex	80–82	13–14	4–6	–	–
Resins	75.7	9.45	14.5	–	0.34

Considerations Concerning the Genesis, Compositions and Structure of Coals

Coal is a castobiolitycal organogene rock, derived mainly from vegetal wastes and their slow enrichment in carbon. In general, in the geological profile, the organic material alternates with other rocks arranged in a certain order, linked to the sedimentation cyclical process. The whole (entire) organic material- inorganic mass could be affected, in some case by orogenetic movements of the earth's crust. Function of the nature of the organic wastes, the accumulation process and the conditions of their transformation, coals are classified into: humic coals, sapropelic coals and liptobiolitycal coals.

Humic coal beds are the most common, so it is usual to assign the term "coal" to different sorts of humic caustobiolites : peat , brown coal, huile, anthracite.

GENESIS:

Excepting the mineral substances, it can be concluded that the carbogenerating substances are: cellulose, lignine, cutine, albumines, fats, resins, waxes. The elemental composition of carbo-generators is present in table 1.

The cellulose $(C_6HNO_5)_n$, representing 60–70% of plant material; is easily chemically decomposed under anaerobic conditions; during the process of formations of coals under anaerobic conditions, the transformation of the cellulose takes place under the action of biochemical factors.

The lignine has a complex structure $(C_{59}H_{50}O_{16}COOH(OCH_3)_6OH$ for pin $C_{49}H_{52}O_{10}C$-$OOH(OCH_3)_2(OH)_2$ for peat and it represents 20–25% of superior plants; it is more resistant in the transforming process than the cellulose, and by oxidation it can form humic acids.

The cutine $(C_{28}H_{48}O_4.5C1_5H_{20}O_4)$ is the equivalent of the cellulose in the epidermal membrane of the cells.

The albumines are azotic substances with sulphure and phosphorus which under anaerobic conditions, under the action of microorganisms are converted into fats. The fats undertake a process of bituminization.

The resins and the waxes are stable substances, which are found in coal.

Therefore, the cellulose and the lignine have the main role in the process of coal generation, the other carbo-generators having a secondary role. Humic acids are the liant between the vegetal substance and the coals. Humic acids of different origin generated by organic wastes of plants present colloidal properties (hidrophilie, dispersion,

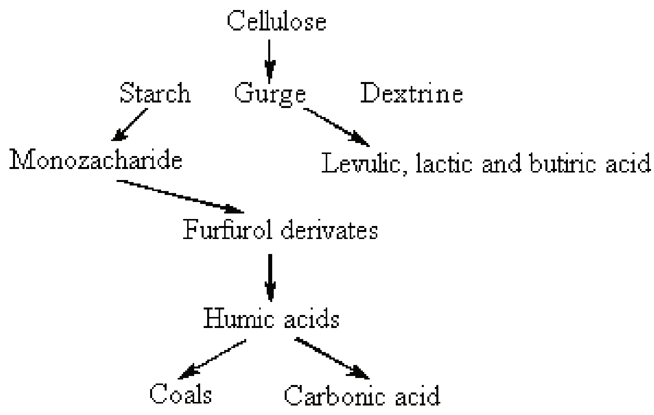

Fig. 1. The generation of coals according to theory of the cellulose

Rys. 1. Powstawanie węgla zgodnie z teorią celulozową

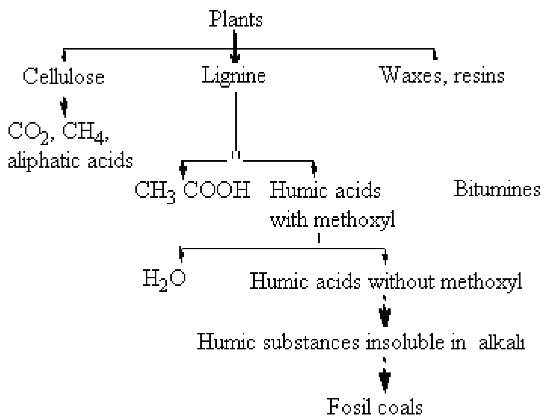

Fig. 2. The generation of coals according to the theory of the lignine

Rys. 2. Powstawanie węgla zgodnie z teorią ligninową

coagulation). Structurally, these are made of polycondensates aromatic nuclea to which metoxyl, carboxyl and hydroxyl phenolic groups are linked, which confer them an acid character; humic acids have bactericide properties. At least half of the lignine from fresh wood is transformed in humic acids by rotting. In the process of cellulose degradation, there has not been observed any generation of humic acids, which means that the humic acids from different species of peat and lignite were formed from the lignine of the plants.

As cellulose and lignine are substances which have the major share in the initial genetic material of coals, and their transformation during the process of generation of coals is realized under the action of microorganisms, the different theories concerning the process of coals generation are trying to highlight these issues.

The theory of the cellulose, represented in figure 1, shows that the cellulose is converted into coal by anaerobic heating at high pressure.

The theory of the lignine, represented in figure 2, shows that during the generation process of peats, cellulose and weaker proteic substances have been transformed under the influence of bacteria; the lignine, the proteic resistant substances and the resins which are transformed in coal are still present.

Theories concerning the influence of microorganisms activity in coal generation process show that in the genesis of different types of humic coals (peat, lignite, anthracite, brown coal and huile) the bacterial activity and the chemical composition of the rocks which form the beds and the roof of the layer have an essential role.

Each of these theories emphasize a number of issues which have a major part in the coal generation from the initial genetic vegetal material, all showing that it is a geological evolution process in the transition from peat to brown coals, huiles

Photo 2. Show the satellite image to Steic Mine

Foto. 2. Obraz satelitarny Kopalni Steic

Photo 3. Aspect from Steic exploitation

Foto. 3. Eksploatacja w Kopalni Steic

or anthracites; the rhythm of evolution is determined by different physical, chemical, biological and tectonic factors.

The carbonization represents the biochemical, physical and chemical evolution of a vegetal layer which is being transformed into coal. The factors, which influence the carbonization, are: temperature, pressure, and duration of the process. The increasing of the temperature plays the main role in transformation inferior coals into superior coals. Pressure acts in the same way as temperature playing a subordinated role, e.g. preventing pyrogenesis production and cocs genesis.

It is noticed that the coal horizontale beds are formed of brown coal, and the coal beds by same age which suffered high pressure are turned into huiles.

There have been a permanent, static pressure due to the layers above the deposit and a dynamic, temporary pressure caused by the orogenetic movements. The increasing of the duration of the carbonization process leads to the increasing degree of coal metamorphozation.

Experimental Part

The following samples have been taken:

1. The lignite sample from current production according to SR ISO 5069-2:1994. The sample from current production was divided into petrographic components (litotypes) based on the characteristics given in geological studies (for Steic coal depots from Oltenia, photo 2 and 3) [6].
2. The detritic coal (DC) which is a fine, humic mass formed by microscopic fragments of carbonized vegetal detritus, with mat aspect, brown (brown-black) color with breakable soil aspect.
3. The xilitic coal (XC) which is distinguished by its woody structure is dirty yellow,

Tab. 2. Results of investigation

Tab. 2. Wyniki doświadczeń

Analysis	Parameter	Work method
Humidity determination in initial sample	W^t_i	SR ISO 1015:1994
Ash determination in initial sample	A_i	SR ISO 1171:1994
Ash determination in anhidric sample	A_{anh}	To be calculated
Fuel mass determination in initial sample	MC_i	To be calculated
Fuel mass determination in anhidric sample	MC_{anh}	To be calculated
Humic acid determination in initial sample	AH_i	SR ISO 5073:1995
Humic acid determination in fuel mass	AH_{mc}	SR ISO 5073: 1995
Elemental analysis function of fuel mass C determination H determination O determination Total S determination Total N determination	 C_{mc} H_{mc} O_{mc} S^t_{mc} N^t_{mc}	STAS 2905-51 To be calculated (by difference) Eschka method Kjeldahl method

Tab. 3. Average results from experiments

Tab. 3. Wartości średnie z eksperymentów

Analyzed parameter	Unity of mesure	Analyzed sample			
		Raw lignite L	Petrographic component		
			DC	LXC	XC
W^t_i	%	40.1	41.3	38.7	27.3
A_i	%	27.3	28.9	20.1	17.2
A_{anh}	%	38.5	40.65	32.79	23.66
MC_i	%	33.1	29.8	41.2	55.5
MC_{anh}	%	61.5	59.35	67.21	76.34
AH_i	%	16.5	17.3	18.54	7.77
AH_{anh}	%	30.62	34.42	30.24	10.68
AH_{mc}	%	49.18	57.8	44.9	13.7
C_{mc}	%	65.12	68.3	56.8	51.2
H_{mc}	%	5.45	5.88	5.58	5.41
O_{mc}	%	24.43	20.29	32.58	39.27
S^t_{mc}	%	2.3	2.68	2.53	2.02
N^t_{mc}	%	2.7	2.85	2.51	2.1

yellow-brown, olive-brown, rarely olive, brown-black color, woody chips breakable and slippery mat aspect.

4. The low xilitic coal (LXC) forms intercalations in the coal layers in alternance with detritic coal stripes, generally xilit milimetric layers.

Work Method

Tests, determined parameters and method of work are presented in table 2.

Results

The obtained results are presented in table 3 as an average of 10 determinations.

The analysis of the obtained results reveal that the raw lignite is a mixture of litotypes with different degree of carbonization reflected in the amount of extracted humic acids and it is a clue of the stadium of metamorphosation.

The participation of these litotypes in generation of raw lignite which is being analyzed is 71.5% detritic coal, 17.8% weak xilitic coal and 10.7% xilitic coal. The elemental analysis for humic acids extracted from each litotypes was made in order to detect the differences between these three litotypes.

In order to obtain a product with appropriate purity (impurities below 0.01%), the humic material obtained according to SR ISO 5073:1995 has been exposed to an additional purification by increasing the time of centrifugation of the liquid phase containing the alkaline hu-

Tab. 4. Separation degree of sodium humate steril function of the centrifugation time

Tab. 4. Stopień oddzielenie humusu sodowego w funkcji czasu wirowania

Centrifugation time (minutes)	Ash (%) contained in sodium humates extracted from			
	Raw lignite L	Detritic coal DC	Low xilitic coal LXC	Xilitic coal XC
5	60.28	72.31	59.37	48.91
10	38.15	52.13	45.30	37.81
15	18.9	22.19	13.43	11.71
20	3.5	3.7	4.23	2.83
25	0.01	0.005	0.007	0.008

Tab. 5. Elementary composition of humid acids (%)

Tab. 5. Analiza elementarna kwasów humidowych

Analyzed parameter	Unity of measure	Source of humic acids			
		Raw lignite	Detritic coal	Low xilitic coal	Xilitic coal
Carbon	%	59.76	63.47	54.53	46.7
Hydrogen	%	5.64	5.78	5.37	4.85
Oxygen	%	28.28	22.6	35.4	47.39
Sulph	%	2.39	2.85	1.58	0.25
Azot	%	3.93	5.3	3.12	0.31

Photo 4. Selective exploitation of Steic Mine

Foto. 4. Selektywna eksploatacja w kopalni Steic

mat and the solid phase made by inert mass of fuel.

The degrees of impurification with sterile of the sodium humates separated by centrifugation function of the centrifuge time are presented in table 4. The amount of steril remaining in dispersion have been determined according to SR ISO 1171:1994 after drying the sodium humates in the stove until a constant weight.

The results of the elementary analysis of the humic acids extracted from all the four samples are given in table 5.

Discussions

The chemical composition of the lignine and the litotypes is different and it is reflected in the elemental composition of extracted humic acids. The different degree of metamorphozation is the cause of these differences. The less metamorphosed litotypes is the xilitic coal which also contains the less amount of extractable humic acids with alkali content (in sodium hydroxide), 13.7% as compared to 57.8% AHmc for CD.

The detritic coal contains the largest ratio of extractable humic material in alkali and the largest quantity of carbon, due to the most advanced degree of metamorphoses. The ratio C/O = 2.8 is the highest for the detritic component as compared to the subunitar C/O ratio for the xilitic component being very close to the C/O ratio for wood, and this confirms once more its low degree of carbonization.

Conclusions

1. Analysis shows that lignite with a high content of xiloidic components is poor in extractable humic acids in alkaline medium.
2. In order to use the lignite in the extraction process of humic acids, it is recommended to be used only the lignite, which contains small quantities of xilitic coal.
3. Taking into account the fact that the exploitable layers of lignite contain different quantities of xilitic coal it is recommended to use poor petrographic component layers to obtain organo-mineral fertilizers with high content in humic acids.
4. Under these circumstances, when the exploitation of the lignite is not a selective one (photo 4), for the processing of the lignite in order to extract humic acids, the xilitic component must be separated taking into account the properties of this petrographic component (namely, increased grinding resistance, lower specific weight, lower friction coefficient). This ratio can be directed in order to process and obtain a cheap active coal, thermal isolation panels, or as solid fuel with high calorific power (almost double as compared to raw lignite).

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Zależność zawartości kwasów huminowych od lignitu ze złożą Oltenia,
znaczenie skladników makropetrograficznych (litotypów)

Drewno węgla brunatnego (lignitu) z pliocenu ze złoża Oltenia (foto. 1) podzielono na trzy składowe w makro petrograficzne, litotypes i analizowano w celu określenia różnic w zachowaniu, które występują w zależności od eksploatowanej warstwy. Do analizy wybrano kwasy huminowe wyodrębnione z węgla brunatnego, jako główny czynnik wpływający na brykietowanie bez lepiszcza oraz właściwości nawozowe w żywieniu roślin i polepszenia gleby. Nie stwierdzono istotnych różnic związanych z wiekiem powstawania (poziom procesu uwęglania) jak również struktury petrograficznej eksploatowanej warstwy węgla.

Słowa kluczowe: lignit, kwasy humusowe, litotypy