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THERMAL CHARACTERIZATION OF HUMIC ACIDS AND OTHER COMPONENTS OF RAW COAL

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Over the ages, the deposits of dead vegetation buried by rock and mudflows, compacted and compressed out all of the moisture; it slowly carbonized and became coal.

Humic acids are natural organic acids – brown coloured biological macromolecules, formed in coal by biochemical changes (decomposition, pyrolysis) of lignocellulosic matter.

From lignite coal bed, the humates were extracted in alkaline medium and isolated from the residual fraction. Humic acids were obtained by treating humates' solutions with HCl.

Thermal analysis (TG, DTG, DTA and DSC) was used in order to establish the decomposition and thermal effects of lignite, humates, humic acids and residual matter extracted from Rovinari mines in Romania. A non-isothermal linear temperature regime was imposed to reveal all decomposition steps.

Keywords: *humates, humic acids, lignite, non-isothermal decomposition, water pollution*

Introduction

It is well known that the south-western part of Romania has important reserves of inferior coal. This sub-Carpathic region of the Meridional Carpathians contains lignite at different thicknesses deposits and depths. A thermal plant was constructed exactly upon the coal deposit. Nearby, the miners' city is supplied with water coming from the underground waters below lignite. The area is highly polluted with coal dust from the extraction zone; in the composition of the ashes resulted from lignite combustion there can be found sodium and potassium oxides, in an apparently unharmfull percentage. In this city, the extraction from the underground waters is not sufficient, people usually making stockpiles in big vessels and bathtubs. In order to eliminate possible infestations with microorganisms, the water is chlorinated. By analyzing the water supplies, it was revealed the presence of organic compounds having raw elementary composition which is similar to that of humic acids from the mined lignite in the area [1].

Vegetal matter, through the geological ages and in specific conditions (incarbonization), for transformation into solid fossil fuel is conducted by thermochemical and biochemical reactions [2]. Coal covers a wide variety in its character, due to its position, geological formation and metamorphosis degree [3]. Lignite from the investigated area is in a reduced incarbonization degree and the humic acids in the coaly matter are freely and partially metamorphosed in humines.

Ashes from the thermal plant, which contains 1–2% Na_2O and K_2O, with moisture formed alkaline hydroxides that went through the lignite deposits extracting humic acids, and then were transported by pluvial water into the underground waters. The high dilution made impossible the detection of humites impurities in the water. Under chlorination, the forming of floccules and their precipitation happened.

Using thermal analysis to characterize humates and humic acids from lignite, then the separated coaly matter and sterile, their formation processes may be established, as well as the amount of each fraction and association that appears during the technological process [4, 5]. In the last years, thermal studies were carried out in order to characterize commercial humic acids [6, 7], humic acids from different types of soil [8, 9], water sediments (sea and rivers) [9, 10], fruits, sugar and amino acids [11, 12]. When humic acids were used as fertilizers, soil health state was investigated by new specific thermal and calorimetric techniques [13, 14].

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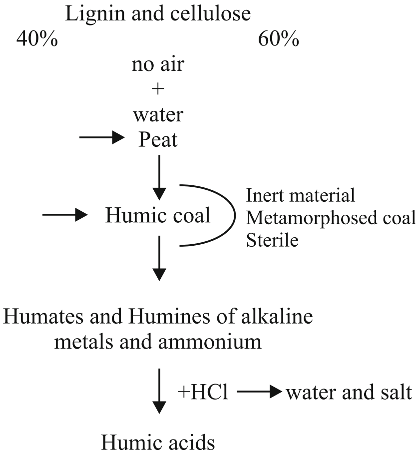

Fig. 1 General scheme to obtain humic acids

Experimental

Extractions of the humic acids from the lignite (Fig. 1) were performed by the treatment with alkaline solutions – in this case, sodium hydroxide. The obtained sodium humates were separated from the combustible and sterile mass by centrifugation [15]. From the soluble sodium humates, humic acids were precipitated by acidification with hydrochloric acid, at a pH value of 5.5. The humic acids are insoluble in water with the pH value lower than 7, so their purification was done by successively washing in bidistilled water and repeated centrifugation. A medium sample was collected from the precipitate in the chlorinated water stockpiles, by centrifugation. The precipitate was washed with bidistilled water until chlorine was eliminated. The precipitate was split in two fractions.

One fraction was treated with sodium hydroxide and thus was completely made soluble, having a typical sodium humate colour.

Thermal analysis of the lignite from Rovinari, ammonium humates, humic acids, coaly matter after the extraction and sterile was carried out in dynamic air atmosphere (150 mL min^{-1}), under non-isothermal regime. A horizontal Diamond Differential/Thermogravimetric Analyzer from Perkin-Elmer Instruments was used during the experiments. Samples from 3 to 6 mg, contained in Al_2O_3 crucibles, were heated from 20 to 800°C with heating rates of 2, 5 and 10 K min^{-1}. Similar curves were obtained in all cases.

Results and discussion

The influence of various compounds (aromatics, organic acids, alkanes, ketone, heterocyclic) on humic acids' (from lignite) thermal stability [16, 17], as well as their oxidative decomposition kinetics [18] have been analysed.

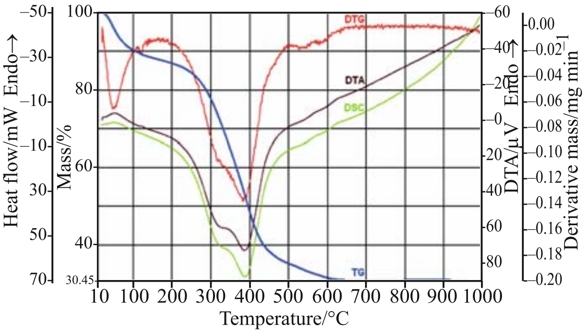

Fig. 2 Thermoanalytical curves of the non-isothermal decomposition of lignite sample (Rovinari mine), recorded at 10 K min^{-1}

Lignite

The lignite mining from Rovinari in southwestern Romania contains about 11–12% humidity water. Up to 105°C (Fig. 2), the thermograms indicate the loss of the absorbed water (first endothermic peak in the DTA and DSC curves), followed until 110°C by the elimination of the structural water. The rest of 2–3% of water is due to the organic functions. The pyrolysis of the carboxylic groups and small catenae (known as 'volatiles') takes place in the temperature range 200–320°C.

The start of the carbon's burning can be seen from the differential caloric and thermal curves, undergoing from 320 to 550°C. After 500°C, DTG curve indicates two exothermic reactions, corresponding to the oxidative decomposition of resin type and metal-sulphide compounds. A residue of approximate 30.5% remains at the end of the non-isothermal investigation above 650°C.

Ammonium and potassium humates

The extraction of humates from lignite was made in alkaline medium, with NH_4OH and KOH. The humates were separated from the combustible matter and sterile by centrifugation.

Figure 3 reveals the non-isothermal decomposition of the ammonium humates, performed in dynamic air atmosphere. As in the previous case, the system loses the absorbed water from room temperature to 100°C. The thermoanalytical curves do not indicate the presence of any structural water. In the temperature range: 100–300°C, the endothermic mass loss is due to the elimination of ammonia and hydroxyl functions from organic compounds. From 300°C, after the elimination of ammonia, the rupture of the lateral organic catenae takes place until 380°C. The pyrolysis of fulvic volatile matter undergoes from 380 up to 420°C. Between 420 and 480°C, the exothermic

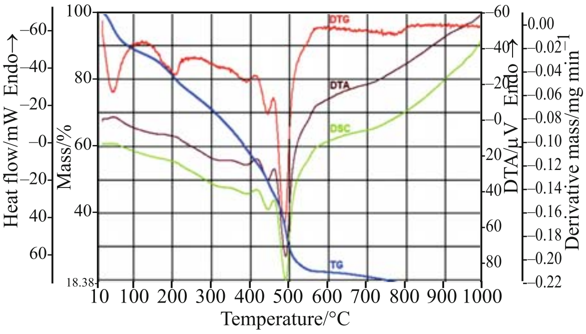

Fig. 3 Thermoanalytical curves of the non-isothermal decomposition of ammonium humates extracted from lignite (Rovinari mine), recorded at 10 K min^{-1}

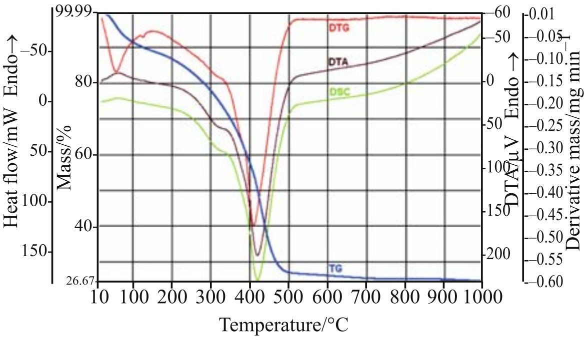

Fig. 4 Thermoanalytical curves of the non-isothermal decomposition of potassium humates extracted from lignite (Rovinari mine), recorded at 10 K min^{-1}

DTA and DSC peaks are the result of the formation of nitrogen oxides. Also intercalated, is the combustion of the coke (450–570°C).

Comparing with the thermal decomposition of the ammonium humates, the decomposition process of potassium humates is much simple because of the absence of ammonia groups (Fig. 4). Between room temperature and 110°C, the system losses the absorbed water. Because of the potassium presence in the humates' molecules and excess in KOH (crystallization water), the structural water is better bonded than in ammonium humates case. The loss of structural and crystallization water (small DTG peak) becomes shifted to higher temperatures (110–115°C). Next mass loss corresponds to the hydroxyl functions from organic compounds (120 to 160°C). The pyrolysis of the volatiles from the potassium fulvates takes place in the temperature range: 160–320°C, followed by the combustion of the coke, at lower temperatures (320–520°C), catalyzed by the potassium cations [19].

After 550°C, DTG curves (both ammonium and potassium humates) indicate a continuous mass loss, corresponding to the same oxidative decomposition of resin type and metal-sulphide materials from the remaining lignite, this time much less intense.

The residual mass percentage differs from ammonium humates (18.5%), when the ammonia is lost, to potassium humates (25%), when the potassium oxide forms. The remained inorganic residue (but less than the residue corresponding to lignite), due to the technological work method employed (centrifugal separation), proves one more time the high amount of solid pollutants in the tap water.

Humic acids from potassium humates

Through the acidulation with HCl of the potassium humates, humic acids were obtained. As mentioned in the experimental part of this paper, the humic acids beeing water-insoluble, have been separated and purified by successive washing and centrifugation. This procedure leads to the removal of fulvic acids.

One must mention the presence of transitional metallic oxides that catalyze the thermal decomposition of carboxylic groups, the pyrolysis of volatiles and carbon combustion. The carbon leaves as oxygenated compounds (200–450°C) while the coal does not accomplish a full cocsification (last peak of the DTG curve in Fig. 5), and what is left burns after 450°C.

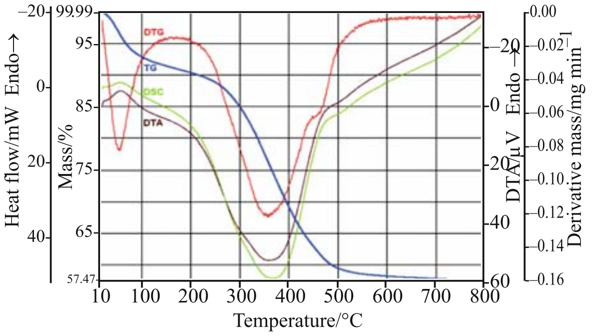

Fig. 5 Thermoanalytical curves of the non-isothermal decomposition of humic acids obtained from potassium humates (Rovinari mine), recorded at 10 K min^{-1}

Coaly matter and sterile

Thermoanalytical curves of the coaly matter separated from potassium humates (Fig. 6) preserve the characteristics of brute lignite (volatiles burning: 180–380°C and coke burning: 380–530°C), but concentrate a higher amount of oxides and carbonates, which endothermic react (620–700°C).

Due to the less content in organic compounds of the coaly matter, the obtained residue (58%) is higher than that one obtained after the thermal treatment of Rovinari lignite (30.5%).

The inorganic part, separated from the coaly matter (sterile) should be inert during heating. But, because of the gravimetric separation only, the sterile

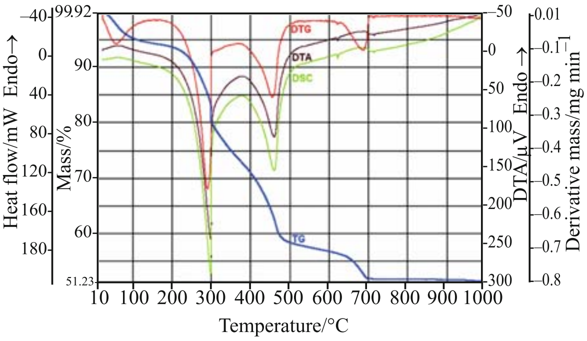

Fig. 6 Thermoanalytical curves of the non-isothermal decomposition of coaly matter separated from humic coal (Rovinari mine), recorded at 10 K min^{-1}

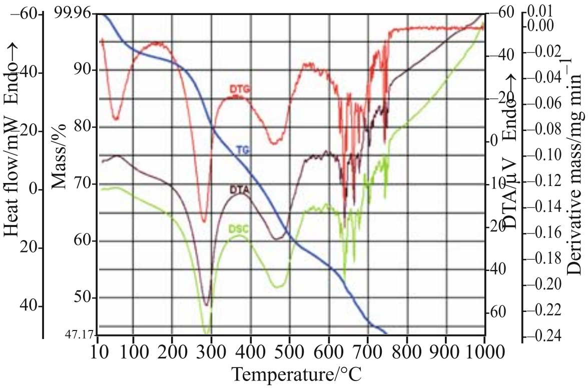

Fig. 7 Thermoanalytical curves of the non-isothermal decomposition of sterile, inorganic part of the coaly matter separated from lignite (Rovinari mine), recorded at 10 K min^{-1}

retained different amounts of coaly matter; characteristic thermal behaviour of organic compounds and coke – DTA and DSC exothermic peaks in Fig. 7.

The mass of the residue after calcinating the sterile (43%) should be higher than that one after burning the coal matter (52%). Inside the aggregations of sterile, coal was assembled, and is released only at precise temperatures (higher than 600°C and depending on the increasing pressure and grain constitution), when the agglomerations are breaking.

Conclusions

Thermal analysis was used in order to characterize the lignite from Rovinari mine, humates and humic acids formation from lignite and also their separation from coaly matter and sterile. Through thermal stability studies one can establish the amount of each fraction and the associations that appear during the technological purification processes employed. While the pyrolysis of investigated lignite takes place as in usual cases, humates' behaviour is due to the different cations ($NH_4^\pm$ and K^+) they possess. After the gravimetric separation, the sterile retains different amounts of coaly matter and, inside the aggregations of sterile, coal is assembled. It is released at precise temperatures, only when the agglomerations are breaking. The technological 'purification' of water supplies leaves together humates, humic acids, sterile and coaly matter. By thermal analysis, the identification of the source and the elimination of the pollution can be made possible.

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