

About the humic acids and thermal behaviour of some humic acids

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Abstract

Abstract: In this paper we investigate thermal behaviour of four samples of humic acids: two samples was prepared in laboratory and two samples were commercial humic acids. Thermal analysis measurements (TG, DTG, DTA and DSC) of humic acids were carried out in dynamic air atmosphere. On relate the thermogravimetric and enthalpic effects.

Keywords: Thermal analysis, humic acids.

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1 Introduction

The south-western region of Romania has important resources of lignite (inferior coal). This region contains lignite at different thicknesses deposits and depths [1]. Organic vegetal matter, through the geological ages and in typical conditions, 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 is a reduced incarbonization degree and the humic acids in the coaly matter are freely and partially metamorphosed in humines [1].

Ecological investigations have focused particularly on the effects forest vegetation has on humic substances quality [4], [5]. The quality of humic substances is defined in terms of its potential persistence and sustainability in soil and therefore is of prime interest to know and to evaluate how structural characteristics of humic substances vary with location, climatic changes or each succession stage of plants and animals in any given ecosystem. How the vegetation affects the humification process it is not yet well defined because several factors and mechanisms such pseudo-climatic condition, soil pH, redox potential and types of mineral present in the soil itself influence this process [6], [7].

In this paper we investigate thermal behaviour of some humic acids used as fertilizers, by using Thermo-Gravimetric analysis (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC).

2 About the humic acids

Humic acid is one of the major components of humic substances which are dark brown and major constituents of soil organic matter humus that contributes to soil chemical and physical quality and are also precursors of some fossil fuels. They can also be found in peat, coal, many upland streams, dystrophic lakes and ocean water.

Humic substances are very important components of soil that affect physical and chemical properties and improve soil fertility. In aqueous systems, like rivers, about 50% of the dissolved organic materials are humic substances that affect pH and alkalinity. In terrestrial and aquatic systems humic substances affect the chemistry, cycling and bioavailability of chemical elements, as well as transport and degradation of xenobiotic and natural organic chemicals. They affect biological productivity in aquatic ecosystems, as well as the formation of disinfection by-products during water treatment. Humic substances are complex and heterogeneous mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains (a process called humification). Plant lignin and its transformation products, as well as polysaccharides, melanin, cutin, proteins, lipids, nucleic acids, fine char particles, etc., are important components taking part in this process. Humic substances in soils and sediments can be divided into three main fractions: humic acids, fulvic acids and humin. The humic acids, fulvic acids are extracted from soil and other solid phase sources using a strong base (NaOH or KOH). Humic acids are insoluble at low pH, and they are precipitated by adding strong acid (adjust to pH 1 with HCl). Humin cannot be extracted with either a strong base or a strong acid. Humic substances are highly chemically reactive yet recalcitrant with respect to biodegradation. Most of the data on humic acids, fulvic acids and humin refer to average properties and structure of a large ensemble of components of diverse structure and molecular weight. The precise properties and structure of a given humic substances sample depends on the water or soil source and the specific conditions of extraction. Nevertheless, the average properties of humic acids, fulvic acids and humin from different sources are remarkably similar.

Humic substances are the most stable fraction of organic matter in soils and can persist for up to thousands of years. They arise by the microbial degradation of plant (and possibly animal) biomolecules (for example aromatic lignin polymers) dispersed in the environment after the death of living cells. Humic material is a supramolecular structure of relatively small bio-organic molecules (having molecular mass <1000 Atomic mass unit) self-assembled mainly by weak dispersive forces such as Van der Waals force, $\pi - \pi$, and CH- π bonds into only apparently large molecular sizes. Their dark color is due partially to quinone structures formed at the environmental redox conditions and partially to enhanced light absorption by the strictly associated chromophore.

Recent studies using pyrolysis -FIMS and -GC/MS, multidimensional NMR and synchrotron-based spectroscopy have shown that humic substances possess both aromatic and aliphatic characteristics. The dominant functional groups which contribute to surface charge and reactivity of humic substances are phenolic and carboxylic groups [8].

An example of molecular structure of humic acids is shown in Figure (1).

3 Thermal behavior of some humic acids

Thermal analytical techniques are used to obtain information on physical and chemical properties of a sample as a function of time or temperature. Thermogravimetry (TG) has

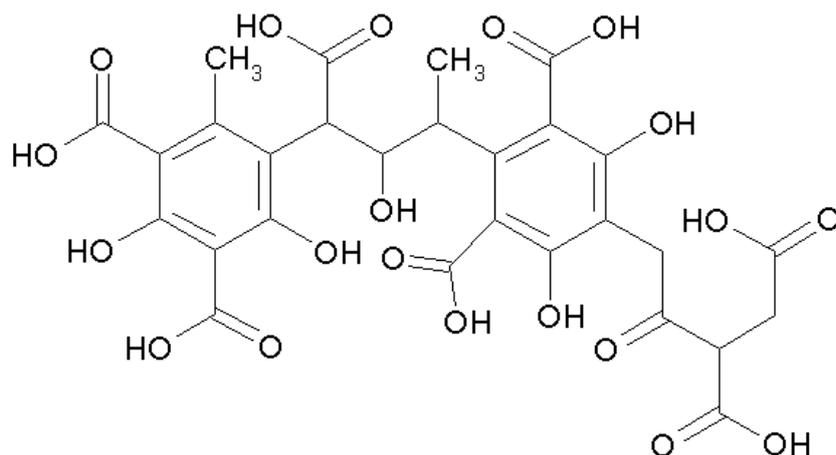


Figure 1: Molecular structure of humic acids

become popular for studying such properties of solids with the advantage in using small samples with temperature control for continuous and simultaneous measurement of weight loss at high sensitivity [9], [10], [11]. The results are quantitative and influenced by heating rate, mass of samples, gas flow rate, sample packing and the gaseous atmosphere [12]. This technique can contribute to understanding the heating effects on soil components such as loss of water, organic matter combustion and clay dehydroxylation, in order to compare the relative abundance of more and less labile carbon sources [13], [14], [15]. The differential scanning calorimetric (DSC) method is convenient for such studies as it is a rapid technique to give characteristic curves, whose variation in enthalpy is associated with phase changes in mineral or soil organic matter, reflecting events related to structures and chemical compositions [16], [17], [18]. Normally, these technique associations offer a convenient advantage to obtain a relatively rapid analysis for trace variations in a given system, originating from different soil samples [19] - [26].

Methods of thermal analysis represent rapid, accurate and interference free approach very attractive also in the investigation of such complex materials as humic acids and related humified substrates [9], [13], [27], [28], [29], [30].

Thermal analysis measurements (TG, DTG, DTA and DSC) of humic acids were carried out in dynamic air atmosphere ($150 \text{ cm}^3 \cdot \text{min}^{-1}$), under non-isothermal linear regimes, using a horizontal Diamond TG/DTA Differential/Thermogravimetric Analyser from PerkinElmer Instruments. Samples at 2.657-6.206 mg, contained in alumina crucibles, were heated in the temperature range of RT-800 °C. Heating rate was $10 \text{ K} \cdot \text{min}^{-1}$. The enthalpic calculations were performed with the specialized software "Pyris".

A comparative thermal analysis of four samples of humic acids was performed. Two samples was prepared in laboratory (S1 and S2) and two samples were commercial humic acids (S3 and S4). Thermoanalytical curves of the samples S1-S4, are presented in Figures (2) - (5).

TG and DTG curves show a continuous mass loss of humic acids. The thermogravimetric effects are presented in Table 1. The thermal effects are presented in Table 2. The gravimetric and thermal calculations were performed with the specialized software "Pyris".

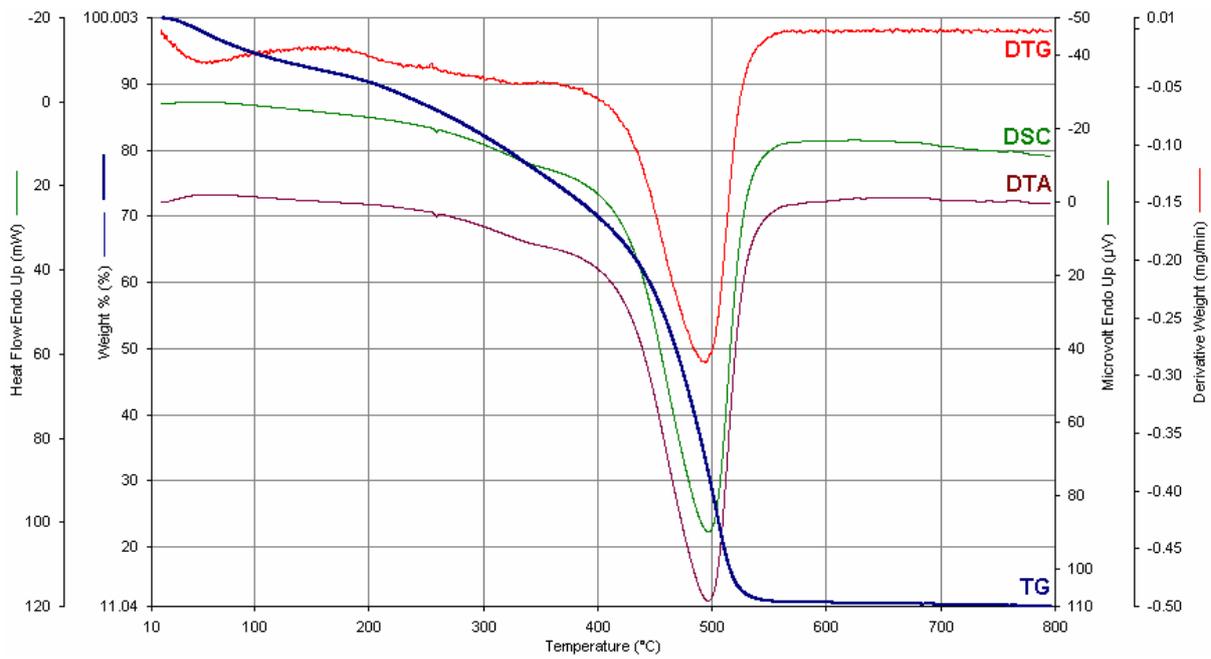


Figure 2: Thermoanalytical curves of the sample S1, in air flow

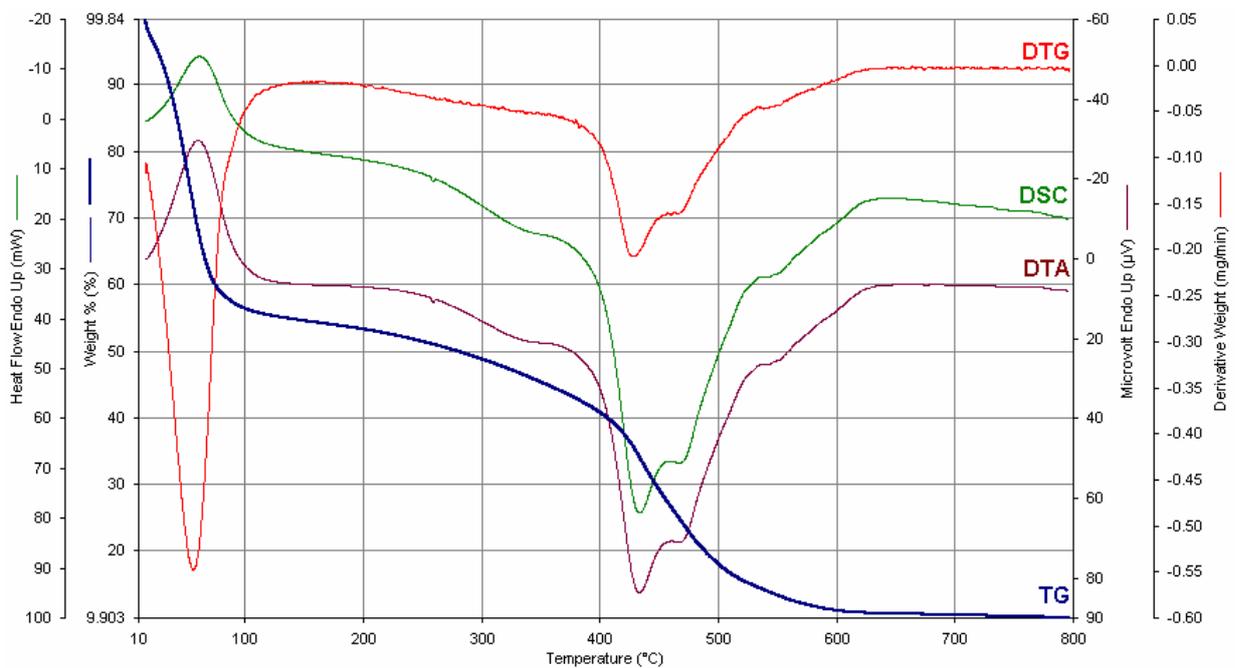


Figure 3: Thermoanalytical curves of the sample S2, in air flow

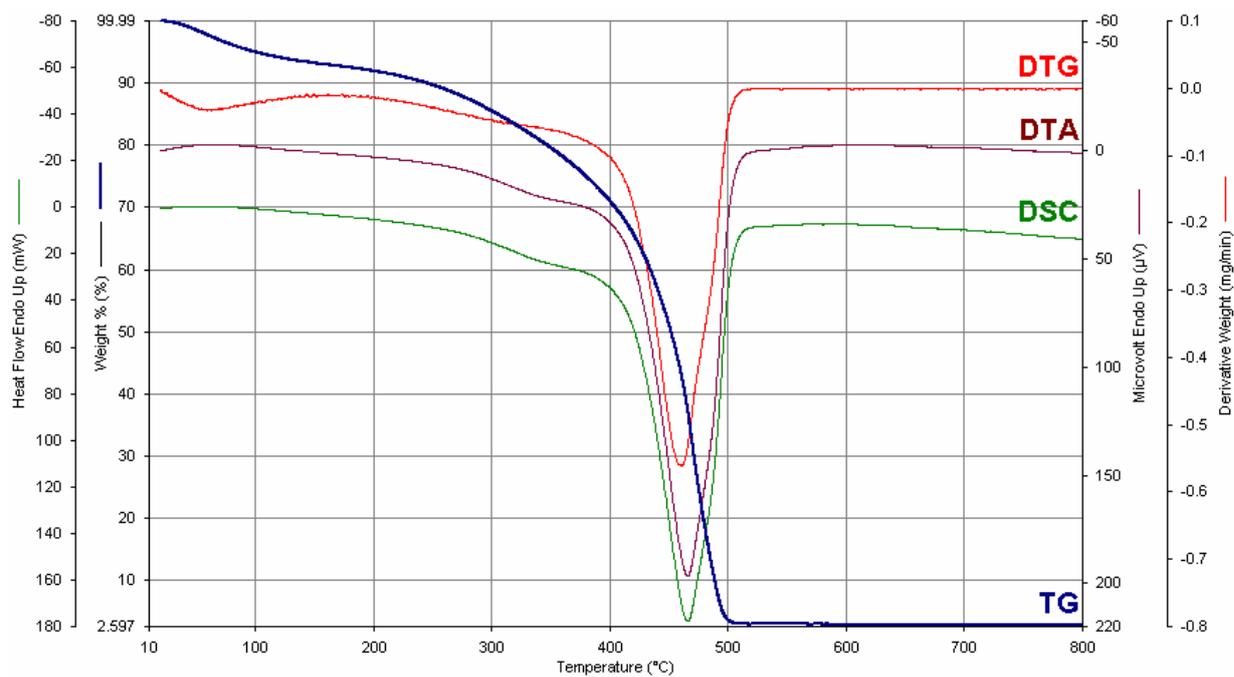


Figure 4: Thermoanalytical curves of the sample S3, in air flow

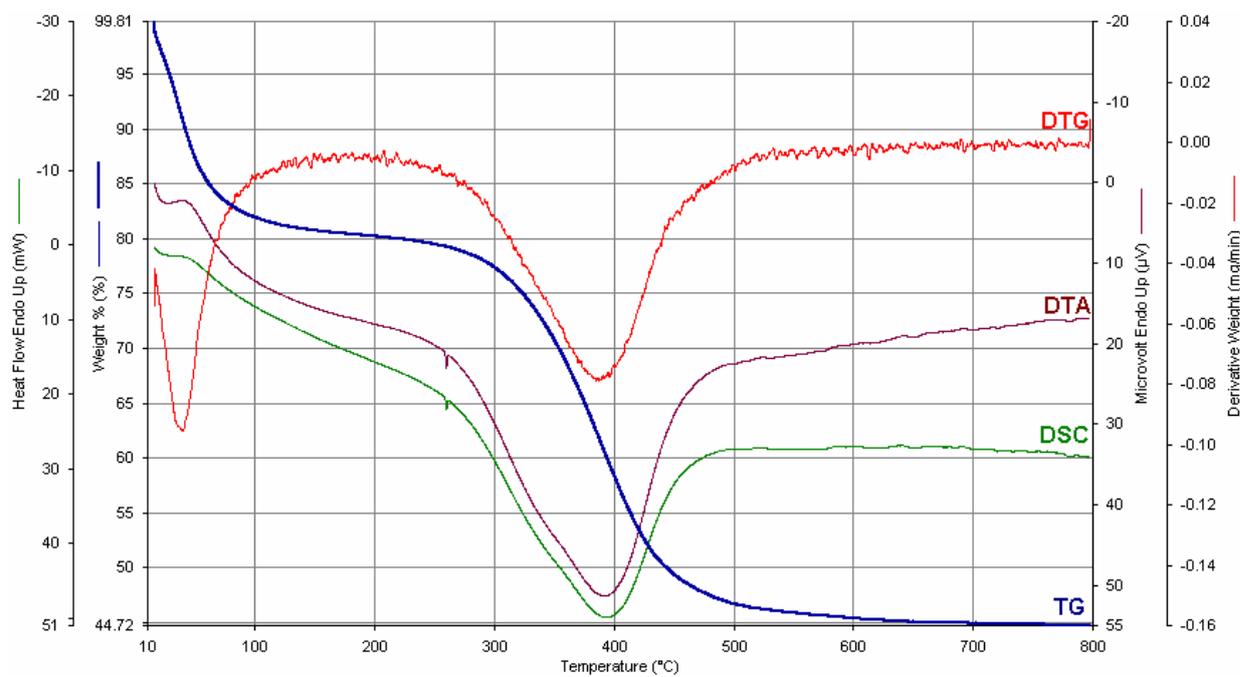


Figure 5: Thermoanalytical curves of the sample S4, in air flow

Table 1 – Thermogravimetric effects

Sample	Temperature of the maximum decomposition rate (°C)	Mass loss (%)	Residue (%)
S1	497.26	88.96	11.04
S2	433.40	90.10	9.90
S3	465.86	97.40	2.60
S4	391.95	55.28	44.72

Table 2 – Enthalpic effects

Sample	Temperature of the maximum exothermal effect (°C)	Onset process (°C)	End process (°C)	ΔH (kJ·kg ⁻¹)
S1	497.26	423.93	529.23	-9794.6
S2	433.40	401.45	523.28	-5410.3
S3	465.86	421.84	503.97	-15684.0
S4	391.95	283.87	454.06	-5675.3

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