Bulgarian Chemical Communications, Volume 43, Number 4 (pp 510 – 515) 2011

Study on thermal stability of composite mixtures on the base of wood ash

M.K. Mladenov*, E.S. Serafimova, Y.G. Pelovski

University of Chemical Technology and Metallurgy, Centre of Ecology, 1756 Sofia, 8, St. Kl. Ohridski blvd.

Received September 4, 2010; Accepted December 8, 2010

The results from thermogravimetric and differential thermal analysis (TG-DTA) of nine composite mixtures, based on ash from burning of wood biomass, green lye from pulp production and ammonium sulphate ($(NH_4)_2SO_4$) – by-product from cleaning of industrial waste gases, are presented. The content of different nutrients and the alkaline reaction of ashes are premise for their use as soil improvers. It is found that oxidation destruction and other reactions take place during the treatment and transformation of some compounds in the primary raw materials. The chemical reactions permit to assess the mixture behaviour in soil systems that refers to nutrients assimilation through the plants roots.

The determined temperature intervals for the transformation of the studied mixtures show that up to 70 °C no gaseous components are released by the nutrients and the studied products are relatively stable. The temperature intervals of the destruction processes occurring by oxidation or dehydration of the mixture components are determined. It is specified that destruction processes take place at higher temperatures, which could be achieved in the soil systems only after incidents with some chemicals or risk situations like fires.

Keywords: wood ash, composite mixtures, thermogravimetric and differential thermal analysis (TG-DTA), waste, soil improver

1. INTRODUCTION

The generation of solid and liquid wastes during thermal, mechanical-biological or physicochemical treatment of different raw materials or wastes, which include biodegradable components, specify the necessity to search for possibilities for their utilization as a secondary raw material or appropriate components for soils conditioners, with the aim to improve soils characteristics and productivity. Different methods and technologies for treatment and use of wastes from thermal processes of vegetable mass are proposed in some publications of Mladenov *et al.* [1], Artiaga-Diaz [2], Li [3], Soares and Menezes [4], [5], Petkova and Pelovski [6]. Brown [7] has used TG-DTA techniques to study the thermal stability and decomposition processes of some wastes.

In the present work the results of the TG-DTA investigations of composite mixtures based on wood ash, green lye and ammonium sulphate are presented.

2. EXPERIMENTAL

Research object are nine composite mixtures, obtained in quantities of 1 kg each, in presence of different contents of wood ash (WA) and green lye (GL). The wood ash contains: moisture – 0.40 %; organic substance (dry substance) ~ 0.37 %; nutrient elements (in the dry substance) - 0.032 % N, 0.72 % P_2O_5, 2.19 % K_2O, 48.7 % CaO, 1.3 % MgO; heavy metals (in the dry substance) - 2.79 mg/kg Cd, 88.5 mg/kg Pb, 22.45 mg/kg Cr, 17.35 mg/100g Ni, 154 mg/100g Cu, 201.5 mg/kg Zn, 11.25 mg/kg As; others (in the dry substance): 81.5 mg/100g Cl, 500-1000 mg/100g SO_4 and 30 - 300 mg/100g Na. Green lye contains: 5-6 % of organic mass, 17-18 % of active calcium and magnesium oxide, 15-16 % of other oxides. In the latter six mixtures different quantities of ammonium sulphate (AS) were added to compensate for the alkaline character of wood ash. The content of elements in ammonium sulphate used is presented in Mladenov *et al.* [1]. The content of different components in the obtained mixtures is shown in Table 1. All components are previously mixed by mechanical treatment for achieving the needed homogeneity.

Apparatus "MOM", 1500 D is used for the experiments. The apparatus is working in dynamic heating regime. The studies are performed in the temperature interval from 20 to 1 000 °C, with a heating rate of 10 °C/min. The range of the mass

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*To whom all correspondence should be sent: e-mail address: mladenov@uctm.edu.

Table 1. Components content in the obtained mixtures

№	WA, g	WA, %	GL, g	GL, %	AS, g	AS, %
S–1	500	50	500	50	0	0
S–2	550	55	450	45	0	0
S–3	600	60	400	40	0	0
S–4	300	30	400	40	300	30
S–5	450	45	350	35	200	20
S–6	500	50	400	40	100	10
S–7	350	35	300	30	350	35
S–8	500	50	250	25	250	25
S–9	550	55	200	20	250	25

balance is 500 mg, and the sensitivities of the recording device are – 500 µV for the TG curve, 500 µV for the DTG curve and 250 µV for the DTA curve. α-Al_2O_3 (Merck, Darmstadt, Germany) is used like as reference material. The sample mass is 500 mg.

RESULTS AND DISCUSSION

The obtained TG-DTA relationships are presented on Figs. 1-9, and the main results derived from them are given in Table 2.

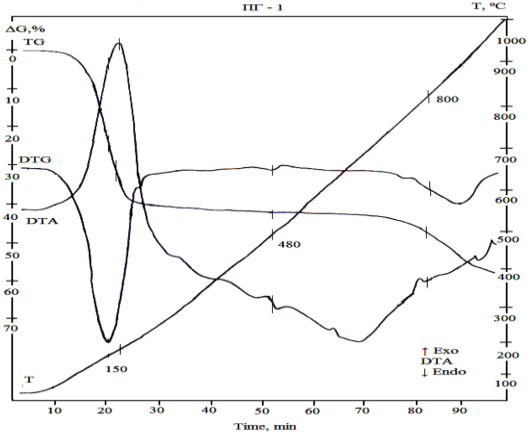

Fig. 1. Derivatogram of mixture S-1.

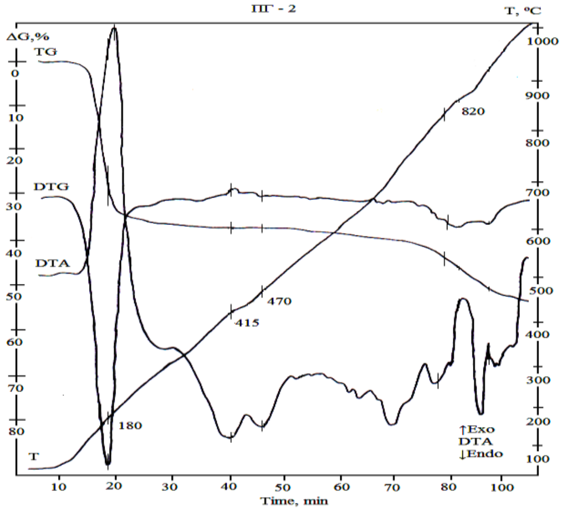

Fig. 2. Derivatogram of mixture S-2.

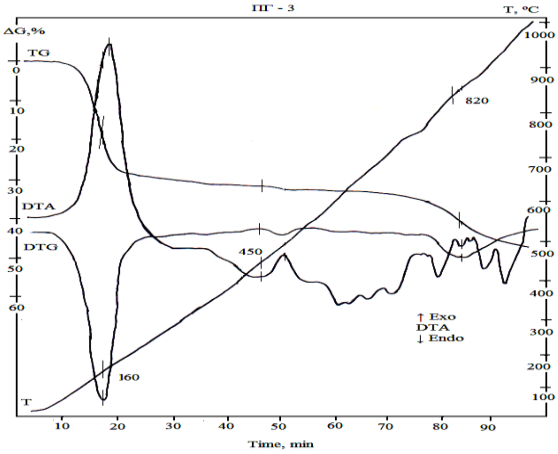

Fig. 3. Derivatogram of mixture S-3

For the mixtures with wood ash and green lye (Figs. 1-3) two main temperature intervals of mass losses are representative – from 45 to 280 °C, where the mass losses are 29.9-30 % and from 790 to 860 °C, where the losses are 2-5 %. The thermogravimetric dependences for the initial temperature interval are typical for auto-accelerating processes, at which mass losses decrease for a lower content of the green lye in the mixtures. The exothermic character of the thermal effect in this temperature interval shows that the mass losses are mainly related with oxidation and generation of gas emission from the organic components in the green lye. Higher mass losses at higher temperatures are registered. Mass losses increase in the same way when the ash content is higher, due to the dehydration and decarbonisation mainly of calcium compounds in the mixtures. This is also confirmed by the registered endothermic effects at the higher temperatures. The range of mass losses in the whole studied temperature range is from 41 to 46 %. The highest total mass losses are registered when the content of green lye in the products is 50 %.

As it is demonstrated on Figs. 4-9, adding of a third component to the system (10-35 % of ammonium sulphate) makes possible the interaction with other components from the mixtures, changing the rate and the character of the processes. The products with the highest content of ammonium sulphate (30-35 %) and green lye (30-40 %) determine the higher level of mass losses and control the rate of thermal decomposition processes. Both the increased content of ammonium sulphate (30-35 %) and the comparatively high content of green lye (30-40 %) show that in such cases no decarbonisation process (Figs. 4 and 7) takes place in the temperature range from 790 to

Table 2. Mass losses at different temperature stages and total mass loses for the studied mixtures.

Mixture	Oxidation of organic component			Dehydration of gypsum and calcium hydro-oxide			Decarbonisation of calcium carbonate			Total mass loses	
	Temperature range, °C	*Inflection point, °C*	*Mass loses, %*	*Temperature range, °C*	*Inflection point, °C*	*Mass loses, %*	*Temperature range, °C*	*Inflection point, °C*	*Mass loses, %*	*Temperature range, °C*	*Mass loses, %*
S-1	50 – 220	150	39.0	470 – 500	480	1.0	790 – 820	800	2.0	20 – 1 000	56.0
S-2	45 – 280	180	36.0	375 – 450 450 – 525	415 470	1.0 0.5	795 – 860	820	3.8	20 – 1 000	53.5
S-3	40 – 220	160	29.9	385 – 480	450	2.0	810 – 850	820	5.0	20 – 1 000	47.8
S-4	50 – 210	160	40.9	450 – 475	460	1.0	755 – 780 780 – 810	770 790	0.5 1.5	20 – 1 000	52.5
S-5	80 – 215	110	28.0	400 – 520	460	1.5	835 – 870	850	4.0	20 – 1 000	44.0
S-6	50 – 170	130	30.4	not detected			730 – 880	800	9.0	20 – 1 000	49.0
S-7	50 – 169	150	22.5	270 – 350	310	3.5	800 – 830	820	2.5	20 – 1 000	41.0
S-8	27 – 180	120	24.5	not detected			700 – 840 845 – 890	760 870	4.5 2.1	20 – 1 000	45.8
S-9	100 – 170	120	11.0	not detected			780 – 860 865 – 910	795 880	6.0 1.5	20 – 1 000	36.7

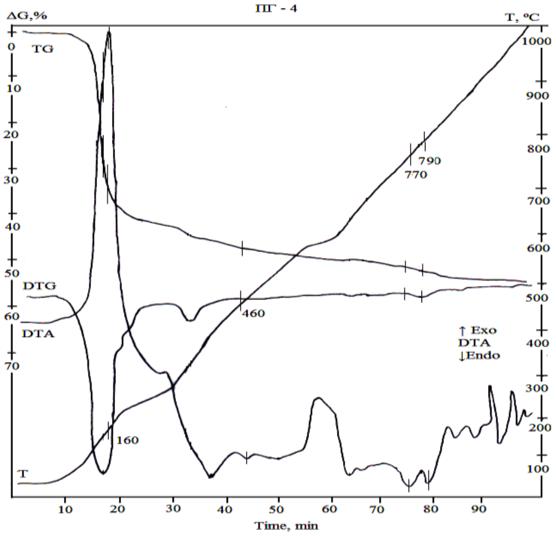

Fig. 4. Derivatogram of mixture S-4

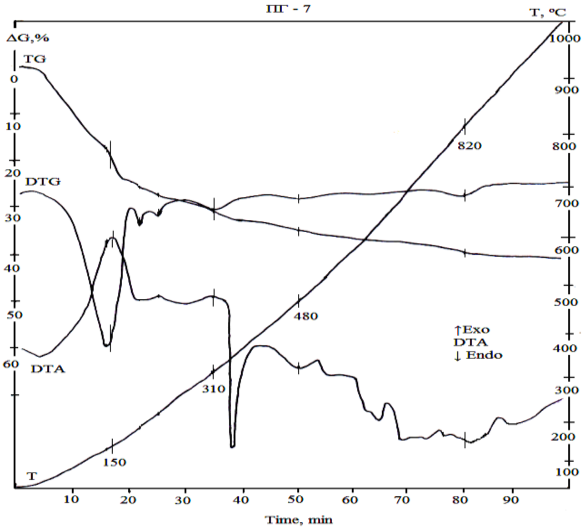

Fig. 7. Derivatogram of mixture S-7.

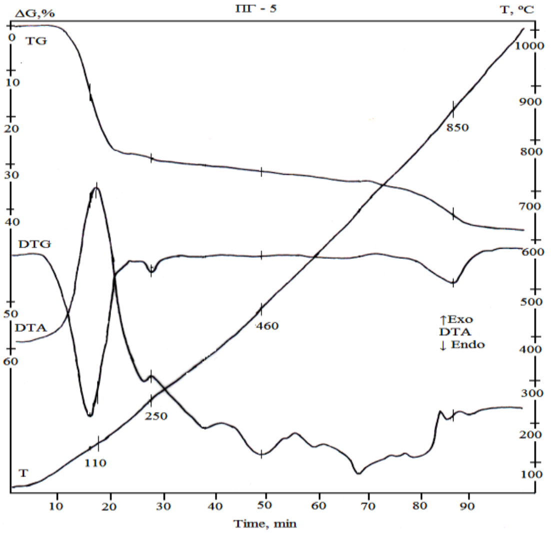

Fig. 5. Derivatogram of mixture S-5.

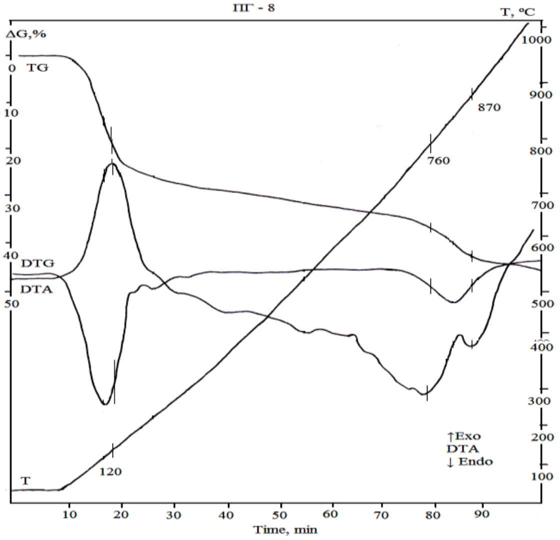

Fig. 8. Derivatogram of mixture S-8.

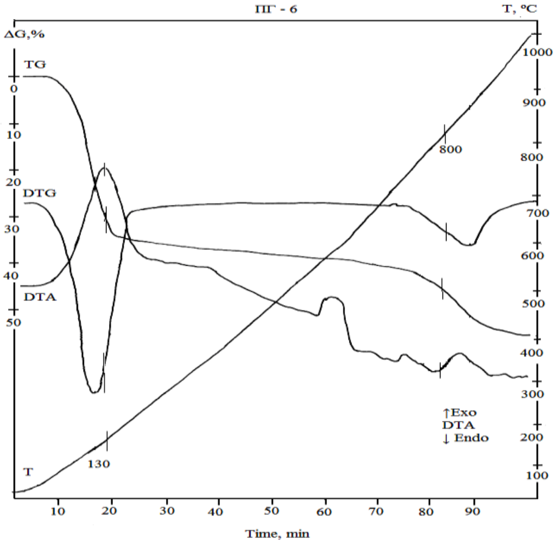

Fig. 6. Derivatogram of mixture S-6.

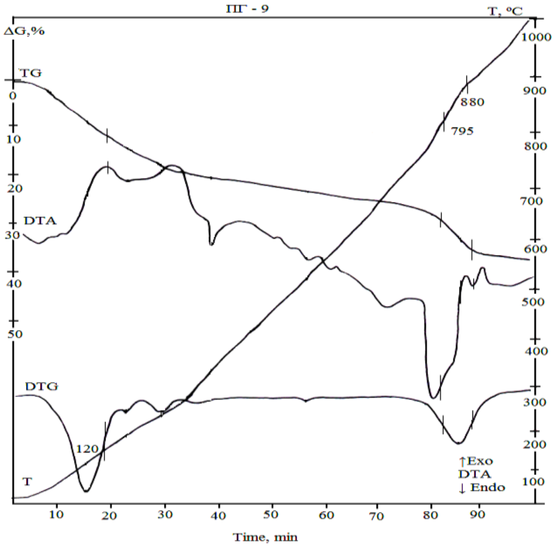

Fig. 9. Derivatogram of mixture S-9

860°C. This may be explained with an exchange reaction during the mixing process between ammonium sulphate and calcium compounds (hydroxide and carbonate).

All products obtained from wood ash, green lye and ammonium sulphate display a typical exothermic process in the temperature interval from 45 to 220 °C. Higher contents of ammonium sulphate and green lye accelerate the decomposition process and increase the mass losses in this temperature range up to 40.9 % for mixture S-4. Decreasing the content of ammonium sulphate to 25 % and green lye to 20 % (Fig. 9) controls mass losses during this stage in the same temperature range and determines lower mass losses – about 11 %. The same relationship is observed for the total mass losses of the mixtures. The total mass losses for mixture S-4 are 52.5 % and for mixture S-9 – 36.7 %.

The main data from TG-DTA studies are presented in Table 2. The weight ratio between the used components controls the temperature range of the reactions taking place and the released gas emissions by the oxidation of organic components in the green lye. Obviously, this is in accordance with the possibility for exchange reactions between ammonium sulphate and calcium compounds in the wood ash, starting with the mixing process.

The TG-DTA studies confirm that during thermal treatment different transformations may take place, changing the phase content of the solid products and releasing gas emissions. The weight ratio between the components in the studied system controls the rate of transformations and the level of enthalpies changes in the system. That allows determining the optimal ratio between the used components with a view to obtain products with desired thermal stability and physicochemical properties as soil improvers.

The obtained data from the investigations done with products from different mixtures and the relationships found permit to determine the main reactions taking place at different stages of the treatments made. The obtained results are in good agreement with the available literature data of Petkova and Pelovski [6], Dweck *et al.* [8], Vedalakshmi *et al.* [9] and Madarasz *et al.* [10]. The main chemical reactions expected during homogenization of the components and investigation of the thermal stability of the products are as follows:

1. Chemical reactions during homogenization:

$CaO + H_2O \Leftrightarrow Ca(OH)_2$

$CaO + (NH_4)_2SO_4 + H_2O \Leftrightarrow CaSO_4.2H_2O + NH_3 \uparrow$

$CaCO_3 + (NH_4)_2SO_4 + H_2O \Leftrightarrow CaSO_4.2H_2O + (NH_4)_2CO_3$

2. Chemical reactions during thermal treatment:

$R\text{-}COOH + O_2 \Leftrightarrow CO_2 + H_2O$

$CaSO_4.2H_2O \Leftrightarrow CaSO_4 + 2H_2O$

$(NH_4)_2SO_4 \Leftrightarrow NH_4HSO_4 + NH_3$

$Ca(OH)_2 \Leftrightarrow CaO + H_2O$

$CaCO_3 \Leftrightarrow CaO + CO_2$

Because of the impurities in the initial components we can not state that the given reactions represent all possible chemical reactions taking place during the processes studied.

CONCLUSIONS

The TG-DTA studies revealed that in temperature range 45 – 260 °C enthalpy and mass losses determine the exothermic oxidation of the organic components coming from the green lye and releasing water vapour and carbon dioxide emissions in the gas phase. At temperatures about 460 °C the processes of dehydration of gypsum and calcium hydro-oxide are completed; in the temperature range 700-910 °C decarbonisation of calcium carbonate takes place. On the base of the results obtained it could be stated that the products are suitable for use in agriculture as soil improvers.

Acknowledgements: *The authors would like to thank the Science and Research Programme (SRC) of UCTM – Sofia for the financial support (Contracts № 10 703/01.02.10 and 10828/ 11.02.2011).*

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ИЗСЛЕДВАНЕ НА ТЕРМИЧНАТА СТАБИЛНОСТ НА КОМПОЗИТНИ СМЕСИ НА БАЗАТА НА ПЕПЕЛ ОТ ДЪРВЕСНА БИОМАСА

М. Младенов*, Ек. Серафимова, Й. Пеловски

Химикотехнологичен и металургичен университет, Център по екология, София 1756, бул. „Св. Климент Охридски", №8

Постъпила на 4 февруари, 2010 г.; одобрена на 8 декември, 2010 г.

(Резюме)

В настоящата статия са представени резултатите от проведения термогравиметричен и диференциален термичен анализ (ТГ-ДТА) на девет композитни смеси на основата на пепел от горене на дървесна биомаса, зелена луга от целулозно производство и амониев сулфат ($(NH_4)_2SO_4$) – страничен продукт от пречистване на отпадъчни индустриални газове. Съдържанието на различни хранителни елементи и алкалната реакция на пепелите са предпоставка за използването им като подобрители за почви. От проведените изследвания се установяват настъпващите процеси на окисление и деструкция на някои от компонентите в изходните суровини и дават възможност да се оцени тяхното поведение и трансформации в почвените системи, имащи отношение и към усвояването на хранителите елементи от кореновата система на отделните растителни видове.

Определените температурни интервали на трансформации в изследваните смеси показват, че до около 70 °C, от формулираните смеси не се генерират газови компоненти на хранителните елементи и не настъпват съществени изменения в структурата на органичните и неорганични компоненти на композитните смеси. Определени са температурните интервали на процесите на деструкция, изразени чрез окисление или дехидратация на отделни фази от композитните смеси. Установено е, че същите протичат при значително по-високи температурни интервали, които в почвените системи биха могли да бъдат постигнати при рискови ситуации на пожари или значимо химическо третиране.