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THE DETERMINATION OF VOLATILE COMPOSITION OF SOLID FUELS BY CHROMATOGRAPHY

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***Abstract*—**The volatile materials released during the heating of solid fuels ignite at relatively low temperatures releasing heat function of their quantity and quality. This heat raises the temperature of the solid residue creating the conditions for his ignition and burning. In the case of burning of the pulverized coal the phenomenon of production, ignition and burning of volatile materials are studied in different articles.

***Keywords*—**coal, fuels, volatiles, wood.

I. INTRODUCTION

THE energy demand of the world is continuously increasing in parallel with population increase and industrial development. Biomass energy is one of the renewable energy sources. When the huge biomass potential of the world is considered, biomass is a candidate fuel to play a supplementary but active role for meeting part of the world's energy demand. Particularly, within the European Union (EU) biomass is seen as the most relevant renewable energy source besides hydropower. Thus, it is expected to contribute substantially to the CO_2 emission reduction targets defined in the Kyoto protocol [1]. Thermogravimetry–mass spectrometry (TG–MS) has been a well-established technique for the analysis of evolved gases since the late 1970s. The main advantage of the technique is to obtain, simultaneously, the information during one TG run such as the weight loss of the sample and the type of the volatile products as a function of the temperature. As to the TG–MS system performance, the following criteria should be met: firstly, a high-flow stability through the TG–MS system is necessary in order to ensure reproducible results; secondly, the intensity of the MS signal should not be affected by the temperature increase in the TG furnace; finally, the intensity of the MS signal should not be affected by the heating rate applied in the TG analysis, in order to ensure that the TG–MS analysis is carried out under chemically controlled conditions [2]-[3]. Combustion characteristics of a fuel before it is used in energy production can be determined by using thermo-analytical techniques such as TG (Thermal analysis), DTG (Derivative Thermogravimetric Analysis), DTA (Differential thermal analysis), DSC (Differential scanning calorimetry) and TMA (Thermo mechanical analysis) which cover a wide range of applications in research, development and economic assessment of fuels. They have been used in a wide variety of areas related to proximate analysis, coal reactivity, and heat effects associated with coal pyrolysis, combustion and heat of hydrogenation [4]. Also was investigated the thermal behavior of loblolly pine. It was described that the energy density of the pretreated biomass could be increased by 8-36%, depending on the torrefaction conditions. Meanwhile, the wet torrefaction process produced a solid with greater energy density than the dry torrefaction at the same mass yield [5]. Several authors [6] carried out the coal combustion in O_2/CO_2 mixtures on a thermogravimetric analyzer and calculated the kinetic parameters which describe the combustion process by linearization using the Coatse method [7]-[8]. Some researches were done to study the combustion behavior and kinetics of four biomass chars, lignite and a hard coal char and their blends. Reaction kinetic parameters were obtained by modeling the combustion of biomass and coal chars as a single reaction, with the exception of lignite and olive kernel chars, the combustion of which was modeled by two partial reactions. A single reaction model was used in the case of coal–wood char blends, while for the lignite–biomass char blends two partial reactions were used. Reactivity was assessed using the specific reaction rate, as a function of conversion. Biomass chars were found generally more reactive than those of hard coal and lignite. The combustion behavior of the blends was greatly influenced by the rank of each coal (hard coal or lignite) and the proportion of each component in the blend. Alteration in reactivity was seen to be more pronounced in the case of lignite–biomass chars than coal–wood chars [9].

A study compared the combustion behavior of lignocellulose materials in CO_2/O_2 and N_2/O_2 atmospheres and calculated the kinetic parameters considering three parallel reactions during the combustion [10]. In this research, thermal characteristics and kinetics of different samples were determined using differential scanning calorimeter (DSC) and thermogravimetry (TG–DTG) at different heating rates. The objective of this research is to investigate the effect of heating rate on the combustion behavior and kinetics of different samples.

II. RESULTS AND DISCUSSION

The quantity and quality of the volatiles can be determined by chromatography. The temperature intervals in which volatiles are liberated are determined using thermogravimetric analysis.

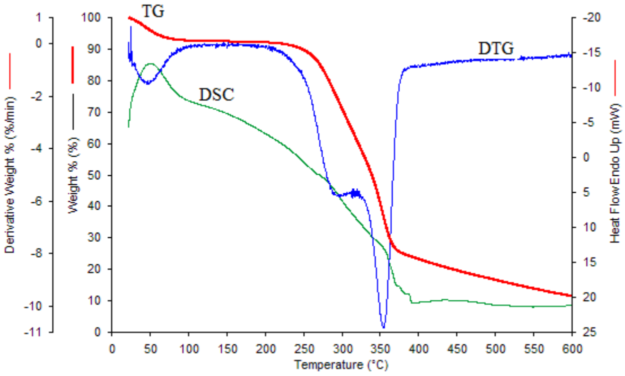

Fig. 1. TG/DTG/DSC curves for oak (recent wood) obtained with a rate of temperature scan of 10 K/min in nitrogen atmosphere

Thermal analyses presented in this paper were obtained for wood (Fig.1, 2), coal (Fig.4) and leaves (Fig.3) from forest tree. The first interval of temperature with mass loss is between 25-85°C, when the water is evaporated and the surface volatiles with low temperature of evaporation. The interval with the fastest rate of evaporation is between 85 and 370 °C. Up to 600 °C all the volatile are evaporated remaining only the carbonic residue, about 12%. The complete thermal decomposition process is presented in table I.

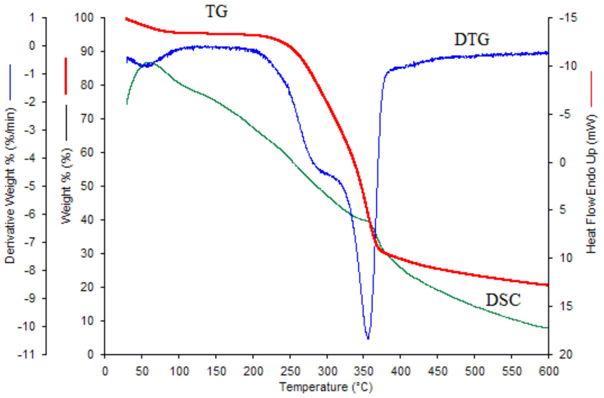

Fig. 2. TG/DTG/DSC curves for beech (old wood) obtained with a rate of temperature scan of 10 K/min in nitrogen atmosphere

TABLE I
THE CHARACTERISTICS OF DECOMPOSITION PROCESS FOR OAK AND BEECH

Oak					Beech				
Interval temp./°C	Effect/ Maximum temp. /°C	Loss in mass/%	Speed %/min	Associate Process	Interval temp./°C	Effect/ Maximum temp. /°C	Loss in mass/ %	Speed %/min	Associate Process
25÷85	Endo 60	8	0,135	Water elimination	25÷85	Endo 75	4	0,071	Water elimination
85÷200	-	0	-	-	85÷200	-		-	-
200÷300	Endo 275	67	0,55	Organic Decomposition	200÷300	Endo 275	64	0,45	Organic Decomposition
300÷370	Endo 358			Sub products Decomposition	300÷370	Endo 358			Sub products Decomposition
370÷600	-	13	0,065	Decomposition/ elimination of sub products	370÷600	-	11	0,046	Decomposition/ elimination of sub products
Final residue at 600°C		12			Final residue at 600°C		21		
Total		100			Total		100		

For thermal analyses of forest leaves are some differences. Between RT (room temperature) and 60°C is noticed a slight reduction of mass (10%) which indicate the water removal and of other substances physical absorbed on the surface of the leaf (gases, such as CO_2, O_2). The mass loss corresponding the 60-110°C intervals represents the structural water elimination and chlorophyll decomposition [10] processes being observed on DTG and DSC curves at 95.1 and 99.8°C ; the processes are overlapping so it is difficult to accurately assign peaks in the thermal diagram. Both processes occur with endothermic effect.

The residue of 8.75% at a temperature of 150°C represents most likely a mixture consisting of organic mass (lignin and cellulose, which decomposes at higher temperatures) and inorganic mass (different metals such as magnesium from chlorophyll structure [11], and other elements like calcium, potassium), also the residue may contain carbon, nitrogen, phosphorus, and sulfur [12] as well as other elements which the plant acquires them from the soil, Fig. 3.

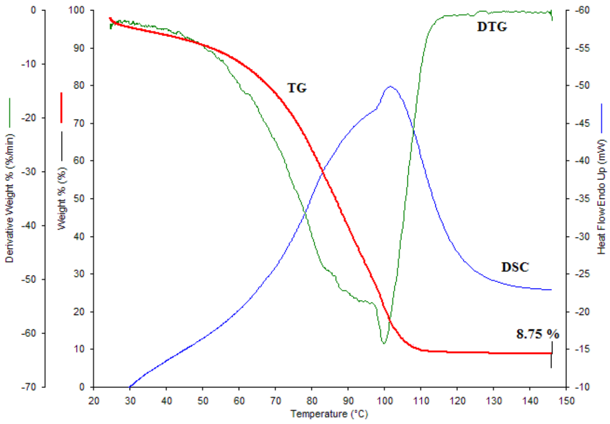

Fig. 3. TG/DTG/DSC curves for leaves of the forest obtained with a rate of temperature scan of 10 K/min in nitrogen atmosphere

For the coal (lignite from Oltenia basin) were effectuated several thermal analyses for different humidity. In the present work the thermal analyses for Rovinari lignite with 22% humidity obtained in static atmosphere of air is presented.

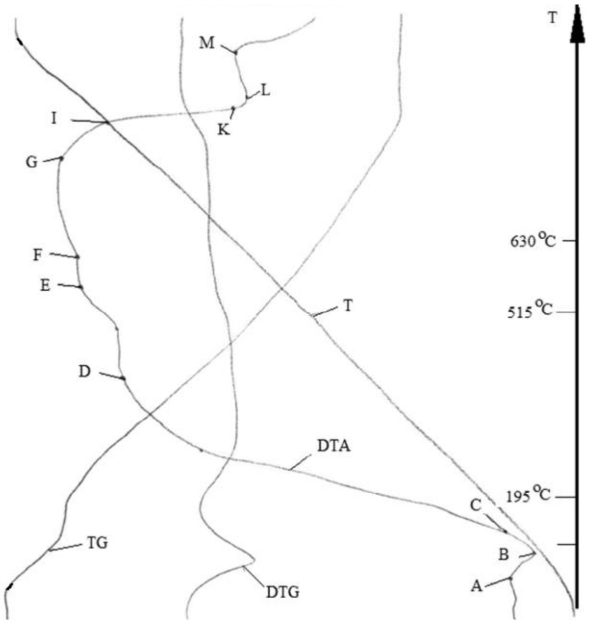

Fig. 4. Thermal diagram of Rovinari lignite with $Wt^i = 22\%$ in static atmosphere of air

TABLE II
INTERPRETATION OF THERMAL DIAGRAM FROM FIG.4

Processes	Wt^i=22 % Static atmosphere of air
Temperature at the end of the drying endothermic process, t_1°C, point C	140
Temperature of the first maximum of volatile evolution, t_2°C, point D	390
Temperature of the second maximum of volatile t_3°C, point E	563
Temperature corresponding the ignition of carbonic residue, t_4°C, point F	630
Temperature in which the quantity of the heat released is less than the heat given to the environment, t_5°C, point I	850

Determination of volatiles composition. For the determination of volatiles compositions were used samples of coal with different humidity and the harvest of the volatiles at different temperatures. The device to obtain the volatiles is a personal conception and is found in the laboratory of Thermal Machines of Faculty of Mechanics of Craiova. The analyses of volatile composition were carried out with a gas chromatograph CARLO-ERBA. The concentration of components has been established considering the high or the surface of the chromatographic peak of the component „i", of $C_i \sim H_i$, where C_i is the concentration of the component „i" and H_i is the high of the chromatographic peak. For the establishment of the volatile participation„i" component, the fallowing relation is used:

$$C_i = f_i H_i A_{ti} \qquad (1)$$

were A_{ti} is the attenuation of the „i" component and is a constant of the apparatus. The „f_i" factors are determined in the calibration process and represents the molecular response factors.

For the determinations effectuated in this paper the factors are presented in table III. The chromatograms obtained are presented below (Fig.5, 6, 7).

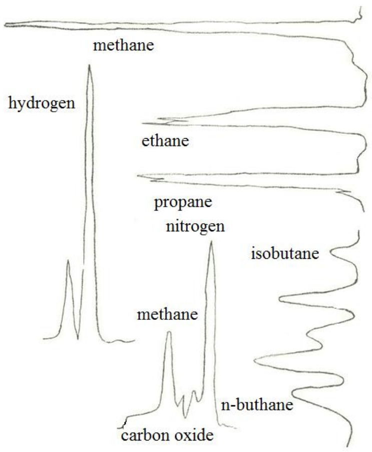

Fig. 5. The chromatogram of the volatiles at 320 °C and total humidity at the initial state of 22%

TABLE III
MOLECULAR RESPONSE FACTORS

Component „i”	Factor „f_i”	Component „i”	Factor „f_i”	Component „i”	Factor „f_i”
C_2H_6	0,0001275	n-C_4H_{10}	0,00022	N_2	0,0069
C_3H_8	0,00009375	CH_4	0,0208	CO_2	0,00735
i-C_4H_{10}	0,00016	CO	0,0142	H_2	0,00025

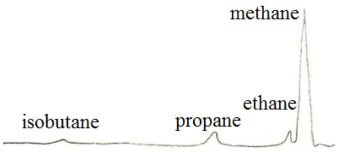

Fig. 6. The chromatogram of the volatiles at 150 °C and total humidity at the initial state of 22%

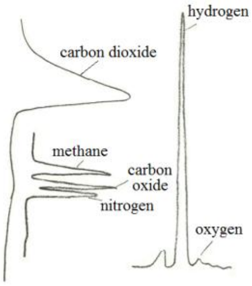

Fig. 7. The chromatogram of the volatiles at 620 °C and total humidity at the initial state of 22%

TABLE IV
VOLATILE COMPOSITION AT 620 °C AND HUMIDITY OF 22%

Component	O_2 [%]	CH_4 [%]	CO [%]	H_2 [%]	C_2H_6 [%]	CO_2 [%]	C_4H_{10} [%]	C_3H_8 [%]	CH_3OH [%]	N_2 [%]
Volume participation	1,07	14,25	10,02	16,38	1,11	38,55	0,023	0,38	1,31	3,49

Volatile mixture has special properties through the participation of hydrocarbons and hydrogen in the ratio of approximately 45% (Fig.8).

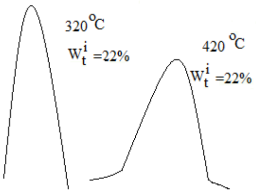

Fig. 8. Carbon dioxide from volatile

Analyses were effectuated for three temperatures for a coal sample with elemental analysis in relation with initial state. The composition of the volatiles is in volume participation reported at the volume of the volatile captured. In table IV it is observed that the mixture formed has high combustible properties through the participation of hydrocarbons and hydrogen.

III. CONCLUSION

The analyses presented in this paper shows possibilities to determine in the laboratory the dynamics of volatile release and their composition. The results obtained in experimental determinations confirm that the statistic relations used in some cases indicate with an acceptable error the volatile composition.

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