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Review

POSSIBILITIES OF USING THERMOGRAVIMETRIC ANALYSIS FOR ENERGETIC

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Energy Engineering brings together a wide range of scientific disciplines. In energetic industry, thermal analysis can be used for determining of properties of fuels, construction materials, seal, ash and others. This research is focused especially on measurement of fuel properties and mass changes of fuel during combustion. As fuel was using biomass, especially it was pellets of rape. Second aim of research is observation of mass changes in ash. Good knowledge of the energy properties of fuels seems to be very important for the proper design of combustion and gasification facilities. Thermogravimetric analysis (TGA) is one of methods of thermal analysis. TGA is one of the advanced methods for testing materials and fuels by temperature increase. In thermo gravimetric analyser, it is possible to simulate thermal conditions which are similar to conditions by combustion or gasification. Thanks to the accurate measurement of weight loss and record of measured data we can deduce changes that fuel material undergoes during these processes.
Key words: Thermogravimetric analysis, water content, content of ash, content of volatile matter, thermal analysis.

Mogućnosti korištenja termogravimetrijske analize u energetici. Energetika okuplja širok spektar znanstvenih disciplina. U energetskoj industriji, toplinska analiza može biti korištena za određivanje svojstava goriva, konstrukcijskih materijala, brtvi, pepela i drugih. Ovo istraživanje je usmjereno osobito na mjerenje svojstava goriva i promijene u masi goriva tijekom izgaranja. Kao gorivo korištena je biomasa, pogotovo su to peleti od uljane repice. Drugi cilj istraživanja je promatranje promjena mase u pepelu. Dobro poznavanje energetskih svojstava goriva od velike je važnosti za pravilno dizajniranje izgaranja i rasplinjavanja sadržaja. Termogravimetrijska analiza (TGA) je jedna od metoda toplinske analize. TGA je jedna od naprednih metoda ispitivanja materijala i goriva pri povišenim temperaturama. U termo gravimetrijskom analizatoru, moguće je simulirati toplinske uvjete koji su slični uvjetima izgaranja ili rasplinjavanja. Zahvaljujući preciznom mjerenju gubitka težine i zapisu izmjerenih podataka možemo zaključiti o promjenama kroz koje gorivi materijal prolazi za vrijeme tih procesa.
Ključne riječi: termogravimetrijska analiza, sadržaj vode, sadržaj pepela, sadržaj hlapljivih tvari, toplinska analiza.

INTRODUCTION

Methods of thermal analysis are used in a lot of technical fields. They are used for detection of the specific properties of materials. It is possible to detect for example composition of samples, thermal capacity, to find the phase changes and others. Probably the most use of thermal analysis is in the field of material engineering, by the development of new types of polymer and composite materials. Power engineering, as a discipline involving knowledge of many different industries, is no exception. This research paper is focused on using of thermogravimetric analysis. Methods of TGA will find their application in testing of fuels, new sealing materials, insulation. In general TGA can be used for measurement of protective and construction materials which requiring high thermal stability.

It is good applicate TGA for material, which is consist from one kind of polymer. The evaluation is different in case analysis of biomass. Because the biomass is composed mainly of three natural polymers. Cellulose, hemicellulose and lignin are the basic building blocks of plant biomass and they are the most common natural polymers on Earth. [1] Every from these three polymers has different properties, it is real necessary to understand the ongoing processes in the fuel during temperature rises. [2] Decomposition processes of these macro-molecular substances are complicated. Every of them have different temperature stability. Lignin has better temperature stability than cellulose and hemicellulose. Otherwise decomposition of hemicellulose begin on the lowest temperature. [3] Difficulty of these polymers are shown on next figures (cellulose, hemicellulose and lignin). A more accurate evaluation requires a good knowledge of the all processes, which occur when biomass is heated up.

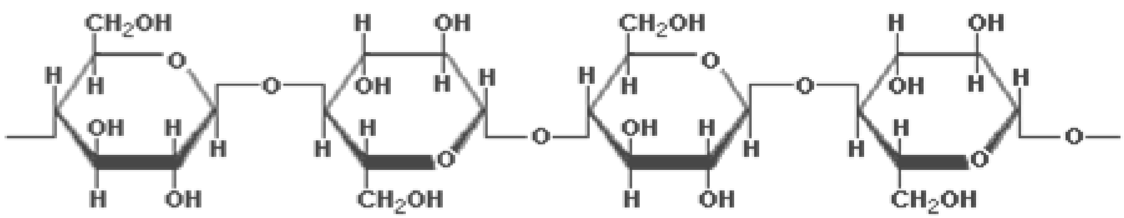

Figure 1. Structure of the cellulose [3]
Slika 1. Struktura celuloze [3]

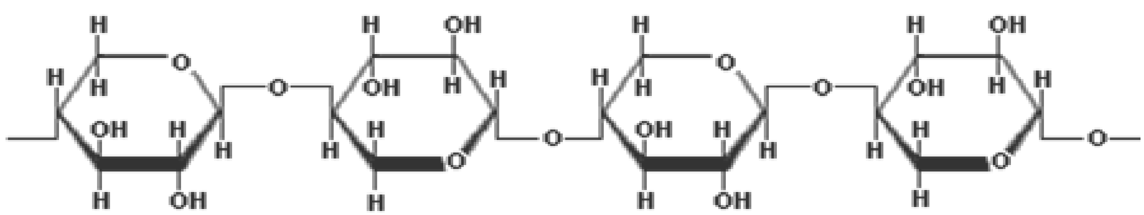

Figure 2. Structure of the hemicellulose [3]
Slika 2. Struktura hemiceluloze [3]

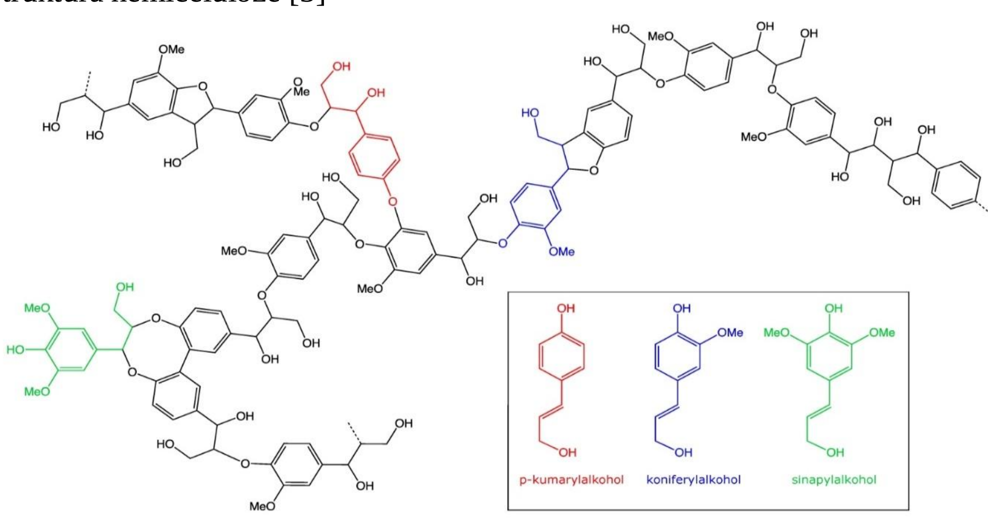

Figure 3. Structure of the lignin [4]
Slika 3. Struktura lignina [4]

THERMAL ANALYSIS

The main purpose of TA methods is to obtain information for the development of technologies for moulding, cooling, heat treatment, forming and other manufacturing processes. These procedures can be optimized based on equilibrium and non-equilibrium diagrams (ARA, IRA, tempering diagrams, kinetic diagrams of eutectic crystallization, etc.). In addition, these methods are used for detection of the degree of phase transformation as well as for the determination of certain physical properties (e.g. melting points of the pure substances, determination of the Curie point temperature of liquids and solids, the coefficient of linear thermal expansion, thermal and electrical conductivity). These methods can also help us in studying of the kinetics and thermodynamics processes and reactions. Thermal analysis can found their place also by controlling the production and the verification of the quality of products. [5]

Depending on the nature of the studied problem, the thermal analysis often combine or complement measurements of other methodologies, such as microstructural and chemical analysis. Interpretation of the results can be facilitated and the amount of knowledge gained significantly extended using a combination of several methods of thermal analysis in a single experiment.

Thermogravimetric combine measurement of temperature and weight of sample. Most commonly occurs to measure of weight loss by controlled temperature increase. Changes inside material structure start during temperature increase and weigh loss due to thermo-chemical changes can be seen as well. The change in mass of the tested sample can be measured either in a continuous increase of temperature (dynamic method) or in isothermal mode (static method).

TGA NETZSCH JUPITER 449

In 2012, thermogravimetric analyser from NETZSCH company Jupiter STA-449 F3 was acquired to the laboratory of the Energy Institute of the project NETME Centre (Fig. 4) It is a well configurable automated analyser with a wide range of uses. The wide range of this device is based on good configurability due to the use of all measuring modules (extensions). When is using a particular module, than it is possible to perform a specific type of analysis. (eg. when is using DTA module, it can perform differential thermal analysis, etc.).

For the time being, the analyser in the laboratories of Energy Institute is time only equipped with TG (thermogravimetric) module. It means that the current configuration of the analyser can measure only the TG signal. TG module has inside only one thermocouple directly under the crucible with testing sample. It is necessary for differential thermal analysis measured temperature of the sample and temperature of reference sample (measured of temperature difference). With only one thermocouple and c-DTA software can be computationally determined c-DTA values (so-called "virtual" DTA-signal). The result of using this computational adjustment is approximate DTA signal without the necessity of hardware expansion of analyser. [6] Temperature of sample and temperature in the furnace are used for calculation c-DTA.

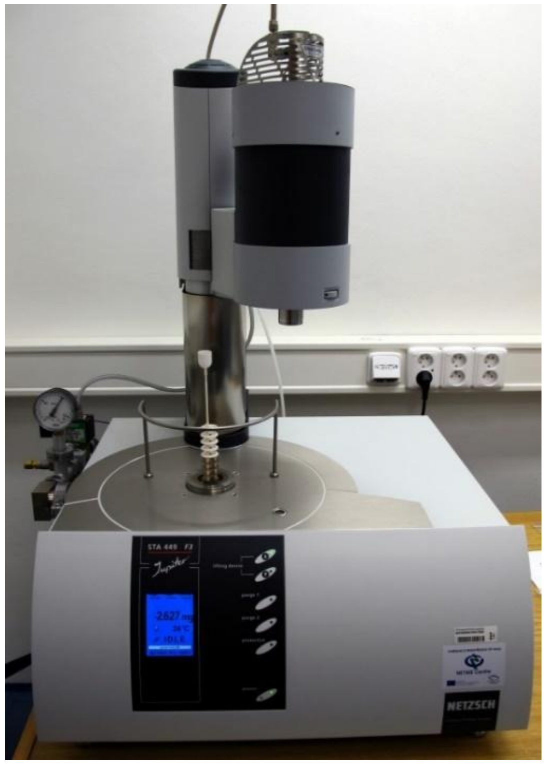

Figure 4. Analyser from company NETZSCH Jupiter STA-449 F3
Slika 4. Analizator tvrtke NETZSCH Jupiter STA-449 F3

Description of analyser

The basic building component of analyser STA-449 Jupiter is a highly accurate digital weighing system with a vertical design. The weighting system is connected to a shielded ceramic module (TG-module), in which the samples for analysis are placed. Before the measurement whole module with sample is inserted into the gas-tight laboratory furnace with controlled heating rate. The ceramic module provides shielding of thermal radiation from a hot oven to sensitive weighting system. Due to protect weighing system from the adverse effects of high temperature.

The furnace for heating up of tested samples is gas-tight. It allows testing of samples by different atmospheric composition. To achieve the desired composition of internal atmosphere is using a vacuum pump. With her help we can suck out the air, which gets into the furnace during the placement of the sample. After sucking out unwanted air fills the space required clean gas mixtures. For better purity of the atmosphere in furnace it is better procedure repeated several times.

The accompanying diagram shows the three gas inputs. Two of them are used to create the required atmosphere in a furnace for measurement. It is possible mix the two types of gases. The third gas inlet serves to bring the protective gas into the weighting system. As a protective gas can be used inert gases or nitrogen. The nitrogen is used most frequently.

The gas composition in the furnace of the analyser depends on the requirements of the experiment. By testing of the fuels is most commonly used gaseous composition similar to air. For simplicity, it is used a mixture of nitrogen (N_2) and oxygen (O_2). It is possible easily modify the content of oxygen in the measurement atmosphere. Part of the experiments on Energy Institute is focused on gasification process of biomass. For following this research should be measured thermal changes in fuel by low content of oxygen in atmosphere. This adjustment of atmosphere can simulate conditions by gasification of fuel.

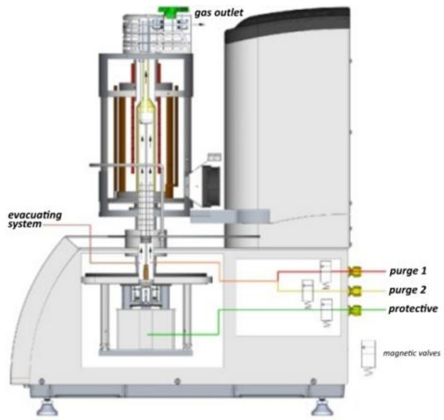

Figure 5. Scheme of analyser Jupiter STA-449 F3 NETZSCH [7]
Slika 5. Shema analizatora Jupiter STA-449 F3 NETZSCH [7]

Technical parameters

Basic technical parameters can show possibilities of the measurement on analyser STA 449 Jupiter F3. Technical parameters say more about conditions, which can be simulated in the analyser.

Table 1. Summary of basic parameters of STA Jupiter 449 F3 NETZSCH [7]
Tablica 1. Opis osnovnih parametara STA Jupiter 449 F3 NETZSCH [7]

Parameter:	**Values:**
Weighting range	35000 [mg]
Precision scales	1 [µg]
Temperature range	20°C (ambient temp.) to 1550°C
Heating rate of the sample	from 0,001 to 50 [°C/min]
Vacuum	do 10 [Pa]
TGA accuracy	to 0,00001 %
Accuracy of temperature regulation	±1°C
Gas-tight furnace guarantee measurement by defined conditions and set the desired atmosphere.	

EXPERIMENTS

TG-time signal is a continuous record of weight loss of the sample due to its heating up. The measured data are for better clarity converted into the graph, where the x-axis is plotted the temperature or time and the y-axis plotting the weight loss (see Fig. 6 and Fig. 7). The measured values of TG-signal themselves do not show anything specific about tested sample. So, it depends on the correctly chosen interpretation of the results, whether to provide requested information and conclusions about the processes inside tested sample.

On Fig. 6 there is the weight loss of the sample during heating up rape pellets in a nitrogen atmosphere. Individual weight decreases indicate the changes in the fuel during the experiment. The first decrease indicates the weight of the evaporated moisture pellets (about 130 °C, 6.13%). The following slow weight decreases show evaporation of aromatic substances. Other abrupt weight loss at about 250 °C indicates the beginning of the evaporation of volatile matter. The total amount of volatile matter is difficult to determine only from the TG-signal. Upon further temperature increase comes into play pyrolysis and the decomposition and evaporation of the other components of the biomass.

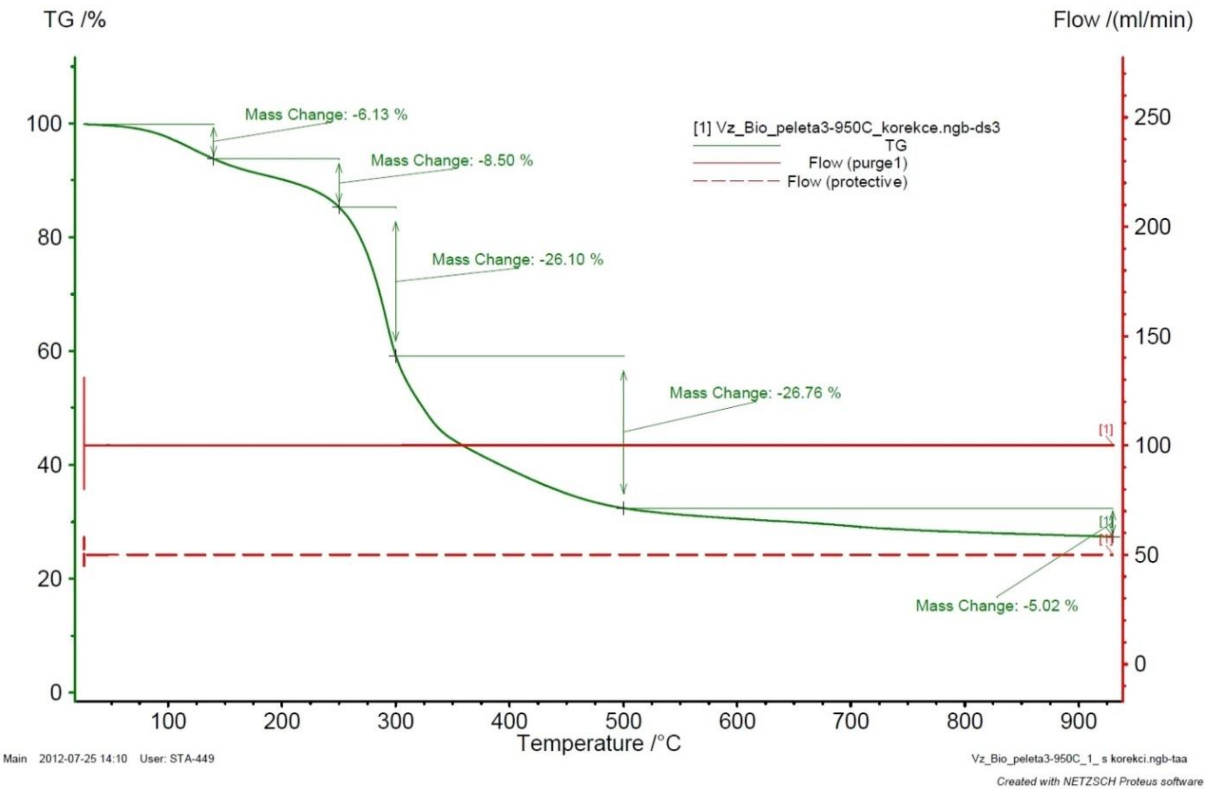

Figure 6. Evaluation of measurement on STA-Jupiter 449, sample was pellet from rape [8]
Slika 6. Evaluacija mjerenja na STA-Jupiter 449, uzorak je bio pelet od uljane repice [8]

For the example TG-signals measured for different materials are shown in the following figures (Fig. 7). This figure shows the behaving of different types of graphite sealing as temperature increases. The aim was to determine and compare the thermal stability of several forms of graphite used as a sealing material. The test was conducted in a simulated air atmosphere (79% N_2 and 21% O_2).

It is clear that changes occur at different temperatures for each material. The start of burning off and even its speed differ for particular types of seals. Material A is the most stable, while the least stable is material E. The seal was not firmly held to the ferrule and there was a large contact surface with the surrounding gas mixture that was the reason why there was such a significant burn off of the sealing material. In real use the seal is firmly clamped between the ferrules and therefore the seal degradation process is slower.

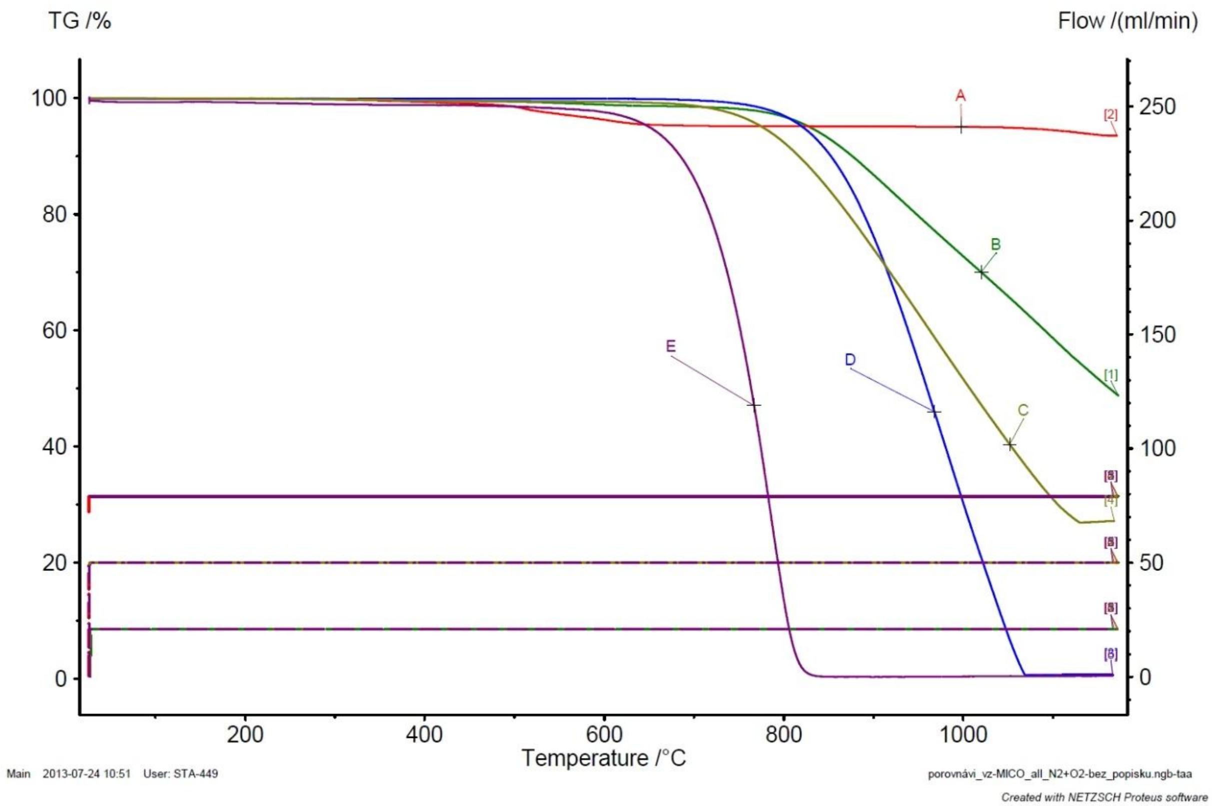

Figure 7. Evaluation of measurement on STA-Jupiter 449, compare of different types of carbon seals by high temperature [8]
Slika 7. Evaluacija mjerenja na STA-Jupiter 449, usporedbe različitih vrsta ugljikovih brtvi pri povišenoj temperaturi [8]

CONCLUSION

Methods of thermogravimetric analysis seem to be good applicable in analysing of the fuels and the materials tested for energy industry. The problem remains how to correct evaluate of the measured signal from TGA. The analyser make only an experiment at pre-setting conditions, but the relevant evaluation of the measured values must make operator of the analyser. Measured values can be processed in different ways than the results of experiments can be differently interpreted. It is necessary to make the entire range of measurement and evaluation to achieve required levels of interpretation of TG-signal. The evaluation is improved on the basis of the experience gained. Not less essential part of the proper evaluation of the measurement is a good understanding of the thermo-physical and thermo-chemical processes in the sample during the experiment. This information and experience can be obtained only by practicing measurement and thorough study of the reporting process.

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