Full Length Article

TSA-MS characterization and kinetic study of the pyrolysis process of various types of biomass based on the Gaussian multi-peak fitting and peak-to-peak approaches

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GRAPHICAL ABSTRACT
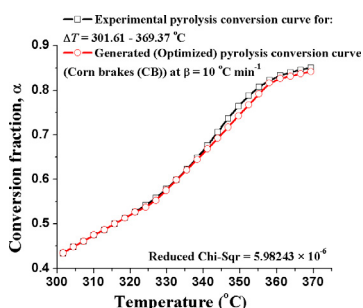
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ABSTRACT

Slow pyrolysis characterization and kinetic modeling study of five different biomasses (corn brakes (CB), wheat straw (WS), hazelnut shell (HS), sawdust (*Beech*), and sawdust chemically treated (SDCT)) were performed in this work, using STA-MS techniques. Thermal decomposition of these samples was divided into three stages corresponding to removal of water, devolatilization, and formation of bio-char. Mass spectrometry (MS) showed that H_2, CH_4, H_2O, CO_2 (C_3H_8), CO, and C_2H_6 were the main gaseous products released during the pyrolysis of biomasses. It was found that H_2O, CO and CO_2 evolutions for all biomass samples arise from lignin source in biomass, followed by the cellulose, and hemicelluloses. It was established that the pseudo-component fraction estimated by the theoretical calculations is dependent on the heating rate. Using Gaussian multi-peak fitting and peak-to-peak approaches, regardless of the type of biomass, it was found that decomposition of lignin occurs independently of decomposition of remaining two pseudo-components and that there is no interaction between them. Namely, it was assumed that during pyrolysis process of biomasses, carbohydrate (hemi-celluloses + cellulose)—lignin chemical structures most likely exist, where the variety of lignin structure units in different types of biomass affects on the level of energy required for its decomposition.

1. Introduction

With much more concern paid to global resources and environment, the utilization of fossil fuels has been greatly limited. As one kind of renewable energy, biomass can achieve zero emission of CO_2 and also can help sustainable development [1]. Thermal chemical conversion

was believed to be the most prominent way for biomass high-efficiency conversion, converting biomass feedstock into gaseous, liquid, and solid energy products under thermal conditions. Several types of technology have been developed, including pyrolysis, gasification, combustion, etc., with controlling the process parameters. Pyrolysis is the most basic process in thermal chemical conversion of biomass, and it also the original and accompanying reaction in gasification and combustion [2–4]. The analysis of pyrolysis of biomass is helpful for the control and optimization of an efficient biomass thermal chemical conversion process.

The pyrolysis kinetics analysis is one important tool for description of the effect of the process parameters on the feedstock conversion process [5]. Study of the kinetics of biomass pyrolysis is of the great importance, because it constitutes the initial step in the process of combustion and gasification, which have been previously highlighted. With kinetic analysis, the reaction system and mechanism during pyrolysis can be discussed, and some fundamental data of thermal chemical conversion can be provided. Knowledge of the kinetics for thermal decomposition of lignocellulosic (cellulose, hemicelluloses and lignin) materials is a necessary requirement for the design and optimization of reactors, for this is required to know the relevant parameters in the decomposition process, such as the apparent activation energy (E_a), pre-exponential factor (A), and reaction order (n).

Kinetics of pyrolysis is very important factor to be understood, since it determines the composition of end-products, and thus, the utilization options for the observed product as well as, influences the technical parameters of pyrolysis process [6–9]. This later one has significant effects on the economic feasibility of biomass pyrolysis processes, too.

Thermogravimetric analysis (TGA) can be a useful method to assess the kinetics of pyrolytic processes; however, as alone, can not provide all the necessary information. For the best results, more detailed analysis of both the raw biomass material and the end-products is needed. The analysis of pyrolysis gases can provide also useful information in this issue. A spatial thermal analysis (TA) with mass spectrometry (MS) can give very useful information on the kinetics of the pyrolytic process [10], where pyrolysis behavior of different kinds of biomass may varies with composition. The mass spectrometry analysis of the evolved gaseous products generated at the various temperatures with kinetic treatments is informative for the characterization of investigated materials. Also, the mass spectrometry makes it possible to identify a number of gaseous species formed and evolved at that as well as to determine the differences in the thermal behavior of various species examined, as well as the emission profiles of these species depending on their origin.

Because of the different analysis apparatus and mathematics tools being applied, the result achieved from the researchers around the world varies greatly and is even disputed sometimes, which weakens the foundation of the fundamental theory system of biomass thermal chemical conversion. Therefore, in this regard, the efforts were directed to provide some new numerical methods that would more reliably describe the kinetics of the pseudo-components decomposition during the pyrolysis of different types of biomass [11–14].

The main goal of this paper is to provide new details about pyrolysis kinetics of various biomass samples categorized within agricultural and wood by-products, using a newly developed approaches based on numerical deconvolution of pyrolysis rate curves. The pyrolysis processes were monitored by STA (Simultaneous Thermal Analysis) (using a NETZSCH STA 445 F5 Jupiter system) coupled with Mass Spectrometry analyzers, which allows implementation of the gas evolved analysis.

The current approaches include the Gaussian multi-peak fitting and peak-to-peak method directly related to the individual decomposition reactions of biomass pseudo-components (pseudo-component 1: hemicelluloses; pseudo-component 2: cellulose, and pseudo-component 3: lignin). The preliminary kinetic parameters of decomposition processes were estimated and this procedure was based on experimental characteristics/parameters attached to the rate curves. Applied procedures

have proved successful in separation and analysis of the overlapping peaks, which regularly appear on the derivative thermogravimetry (DTG) curves of the biomass pyrolysis. The procedures presented in this work could be applicable to a much wider range of similar kinetic problems.

2. Materials and methods

2.1. Materials and sampling procedure for tested materials

For simultaneous thermal analysis (STA), five different biomass samples were used. Three samples among them are different types of agricultural biomasses: corn brakes (CB), wheat straw (WS) and hazelnut shells (HS). The remaining two samples represent the wood processed products: sawdust (SD) and factory-formed wood product as chemically treated sawdust (SDCT) (treated with an organic preservative – MDF – urea-formaldehyde adhesive).

Corn was grown on domestic fields in central region of the Republic of Serbia. After peeling, corn brakes were left on a pile as industry leftovers for 2 months. Hazelnut shells came from suburban region of Serbia, near Capital city, Belgrade. After removing hazelnuts' inner part, shells were collected in bags and left for 8 months before they were brought to the laboratory. Wheat straw was brought from the mountains in Southern Serbia and it was already dried before sample preparation started. Sawdust was collected from the process of cutting beech log wood for household heating, while the chemically treated sawdust was obtained from local carpenter workshop.

According to standard EN ISO 14780 [15] for solid biomass fuel sample preparation each biomass sample was prepared for experimental tests. Sample was removed from the transportation packing, and then it is placed inside the oven at 105 °C for 2 h, in order to define moisture left on the inner surfaces of the packing. This amount of moisture was included in the calculation of the total moisture content in the sample according to standard EN ISO 18134 [16]. Further, regarding to pre-drying process of the sample, which is necessary to remove the residual moisture during preparation, sample was placed on a plate and left to reach moisture equilibrium with laboratory atmosphere conditions for 24 h. After that period of time, sample was reduced in two steps using cutting mill, after which it was sieved through the 1 mm (18 Mesh sizes) sieve.

Finally, the obtained undersize was declared as a general analysis sample and divided into 3 test portions for further testing. First portion of prepared sample was used for determination of ultimate analysis (carbon, hydrogen and nitrogen content) that was performed at University of Belgrade, Faculty of Chemistry, according to standard EN ISO 16948 [17]. The results of proximate analysis (total moisture, ash, volatile matter and char content) were obtained from the second portion of the prepared sample. This analysis was performed at Fuel and Combustion Laboratory of University of Belgrade, Faculty of Mechanical Engineering, according to standard procedures EN ISO 17225-1 [18]. Also in this laboratory, the higher heating value (HHV) and lower heating value (LHV) for tested samples were determined using calorimeter laboratory equipment with an oxygen bomb (IKA C200, IKA® Works, Inc., Wilmington, USA), according to the standard EN ISO 18125 [19].

2.2. STA measurements

STA (recording TGA-DTG) measurements were performed on the third portion of the prepared biomass sample, and all of the obtained results were used for studying the pyrolysis kinetics.

NETZSCH STA 445 F5 Jupiter system (Erich NETZSCH GmbH & Co. Holding KG, Germany) was used for STA experimental tests for all examined samples. Inert atmosphere was provided to maintain the pyrolysis process using the high purity nitrogen (Class 4.6) as a carrier gas. At the same time, nitrogen was used as a protective gas in order to keep