Characterisation of Various Biomass Waste

Dolinská S.[1*], Znamenáčková I.[1], Lovás M.[1], Briančin J.[1] And Čablík V.[2]

[1]Institute of Geotechnics of SAS, Watsonova 45, 040 01 Košice, Slovak Republic

[2]VŠB - Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu 15, 708 00 Ostrava - Poruba, Czech Republic

*corresponding author: Silvia Dolinská

e-mail: sdolinska@saske.sk

Abstract Agricultural biomass as an energy resource has several environmental and economical advantages and has potential to substantially contribute to present fuel demands. It was well-known that straw and rape residue are a potential sources of energy and value-added by-products among the various biomasses. The results of thermal analysis indicate that thermal degradation of the biomass waste occurs through three steps: decomposition of hemicellulose (220–315 °C), cellulose (315–400 °C) and part of lignin (137–900 °C) and resulted in the formation of char.

Keywords: biomass waste, thermal analysis, FTIR spectroscopy

Introduction

The development and utilization of alternative sustainable renewable and clean energy has been pursed due to the current energy crisis (petrochemical resources) and emerging anthropogenic environmental problems (greenhouse effect, surface subsidence, emissions of trace elements and organic pollutants) (Zhou *et al*., 2016, Demirbas, 2004; Zhou *et al*., 2015). Renewable energy resources, i.e. biomass, hydropower, geothermal, solar, wind and marine energies, have the ability to provide energy with zero or almost zero emissions of both greenhouse gases and trace pollutants (Demirbas, 2005). Among them, biomass as the solar energy presented as chemical form in plant/animal materials (agricultural residues, forestry residues, algae, etc.), is considered as the best substitution of fossil fuels (Lee *et al*., 2010; Piriou *et al*., 2013). Meanwhile, biomass is regarded as the clean and important energy due to the completely CO_2 and SO_x neutrality, available abundantly, renewable potentially and cost-effective (Zhang *et al*., 2013). Moreover, the utilization of biomass may provide an alternative for the disposal of these biomass and their exploitations as energy source (Idris *et al*., 2012). Since the energy crisis in the mid-1970s, the energy utilization of biomass resources had received considerable attention. Biomass was a kind of renewable energy source. The utilization of biomass rather than existing fossil fuels could offer more environmentally acceptable process for energy production and aid in conserving the limited supplies of fossil fuels. The conversion technologies of biomass to energy are mainly combustion, pyrolysis and gasification, biomass can be converted into useful forms of energy efficiently using such processes (Verma *et al*., 2012, Sikarwar *et al*., 2016, Yang *et al*., 2014, Varol *et al*., 2010, Mushtaq *et al*., 2014). Biomass, such as straw, grasses, wood shavings, sawdust, roots, branches, leaves and bark, are used in different forms for energy production. The wheat straw was the main biomass, which was used in the production of heat and power. At present, the utilization efficiency of wheat straw was very low, so the high-efficient and clean technologies for the utilization of wheat straw were greatly encouraged. Wheat straw combustion was different from coal and carbon due to its higher volatiles, therefore it was important to study the combustion of wheat straw. The oxidative pyrolysis kinetics of wheat straw had studied by thermogravimetric analysis (TGA) under oxygen dynamic atmosphere (Cai *et al*., 2009). Thermal analysis techniques had been widely used for combustion and pyrolysis of biomass (Varol, *et al*., 2010, Părpăriță *et al*., 2014, Zhoe *et al*., 2016). The catalysts were used in the process of biomass combustion, which changed the process of combustion, leading to the energy release in short time and avoiding the behaviour of agglomeration. It is propitious to the use of energy.

1. Materials and methods

1.1. Materials

The experiments were realized with the samples of the biomass waste - rape residue and straw waste. The samples were subjected to comminution using the grinder MRC model FDV and in such way grain size was reduced to 1 mm. The chemical analysis of studied biomass samples are in Table 1.

1.2. Methods

CHNS analysis was performed by elementary analyzer Vario MACRO cube (Elementar Analysensysteme GmbH, Germany) using thermal conductivity detector. Helium (purity 99.995 %, intake pressure 2 bar) was chosen as a carrier gas in all analyses. The purity of oxygen for combustion was 99.995 % with intake pressure of 2 bars. Combustion tube was set up to 1150 ºC and reduction tube to 850 ºC. Sulfanilamide (C = 41.81 %, N = 16.26 %, H = 4.65 %, S = 18.62 %) was used as CHNS standard. STA

449 F3 Jupiter thermal analyser was used to study the thermal behaviour of biomass samples. The experiment was done at linear heating rate 5 °C min^{-1} within the temperature range from 40 °C to 700 °C in argon atmosphere. The sample (amount 50 mg) was placed in a Tungsten crucible. The infrared spectra were obtained using the KBr technique using Nicolet 6700 FTIR spectrometer. For each sample 64 scans were measured in the 4000-400 cm^{-1} spectral range in the abs mode with a resolution of 4 cm^{-1}. The overview morphologies and sizes of the particles were obtained by a field emission scanning electron microscope TESCAN MIRA 3 FE SEM with an accelerating voltage of 20 kV. The samples were examined at several magnifications.

2.   Results

At present several technologies are applied in biomass utilization, such as separation, fermentation, pressing, classification and drying.   Full use of biomass and minimization of transportation costs are typical requirements for biomass utilization processes (Fig. 1). Infrared spectra taken from straw waste and rape residue samples are shown in Figure 2 with the bands of interest being identified by their wavenumbers. The broad bands in the 3200–3500 cm^{-1} range are assigned to OH stretching vibrations and at 3000–2800 cm^{-1} to C–H– bonds. Strong signals at 1600–1630 cm^{-1} are assigned to bound water, whereas the 1400 cm^{-1} is assigned to C=O stretching, and the clearly observed peak at 1050 cm^{-1} indicates the presence of C–O and C–O–C bonds. The band at 670 cm^{-1} is characteristic for cellulose and is an OH torsional vibration band. The band at 1160 cm^{-1} is attributed to the antisymmetric stretching of C-O-C glycosidic linkages in both cellulose and hemicelluloses. The band at 1240 cm^{-1} is attributed to the antisymmetric stretching of C-O-C of acetyl groups (Gierlinger et al., 2008). However, for both reference xylans a band is found at 1245 cm^{-1} and is of approximately the same strength as the (xylan) 900 cm^{-1} band. The assignment of the 1240 cm^{-1} band to lignin can also not be ruled out. The peak observed at 1505 cm^{-1} is diagnostic of lignin and is placed in a spectral region devoid of polysaccharide peaks. No clear change of this peak is observed for most of the temperature range. The band at 1732 cm^{-1} is attributed to the carbonyl stretching band of carboxylic acid groups in hemicelluloses. The narrow CH$_2$- stretching bands (superimposed a broader band) at approximately 2850 cm^{-1} and 2920 cm^{-1} are ascribed to the aliphatic fractions of wax (Kristensen et al., 2008). By analysing the FTIR spectra of the biomass samples, it can be concluded that there crease of these bands is suggested for the highest temperatures.
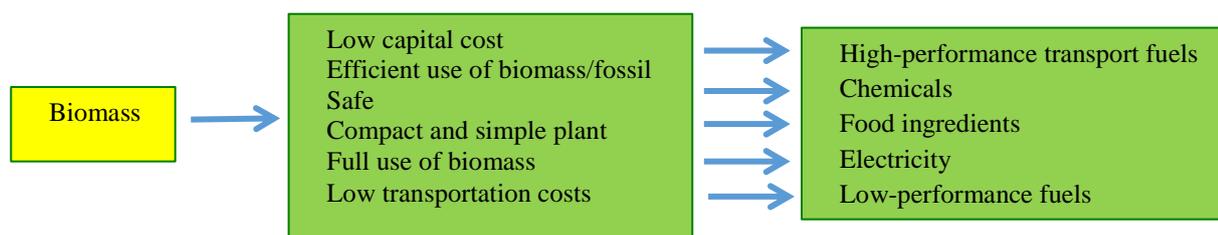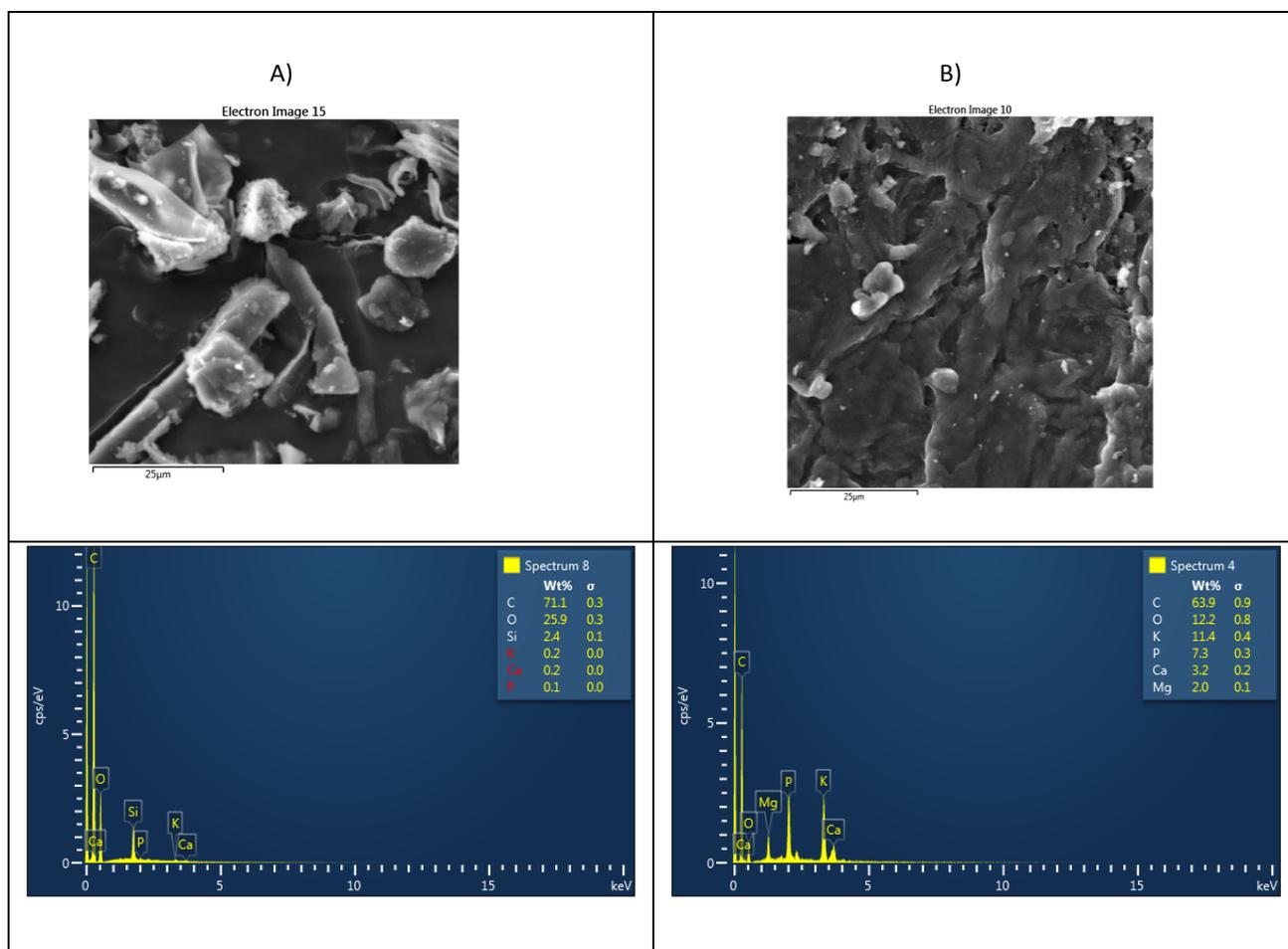

Figure 1. Important requirement for an ideal process for utilization of biomass (Sanders et al., 2012)

Table 1. CHNS analysis of biomass samples

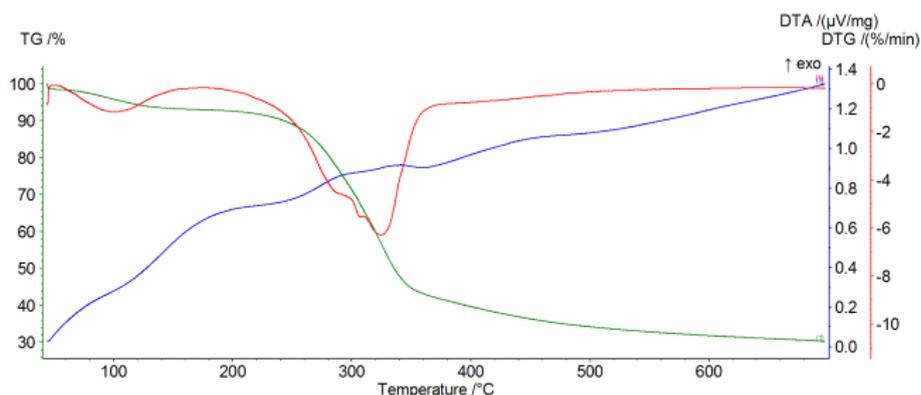| Sample	N [%]	C [%]	H [%]	S [%]	O [%]
Straw waste	1.7	39.7	6.0	0.2	45.1
Rape residue	5.3	46.5	7.4	0.7	37.3
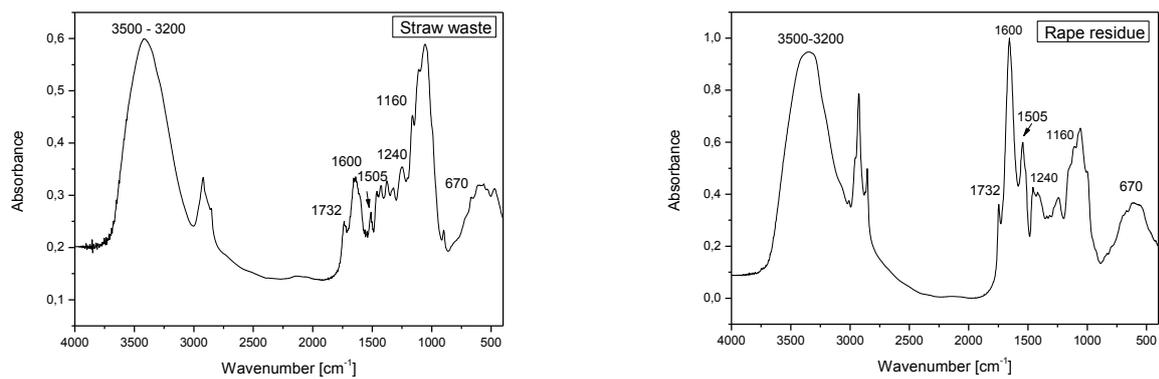
Figure 2. Infrared spectra of straw waste and rape residue
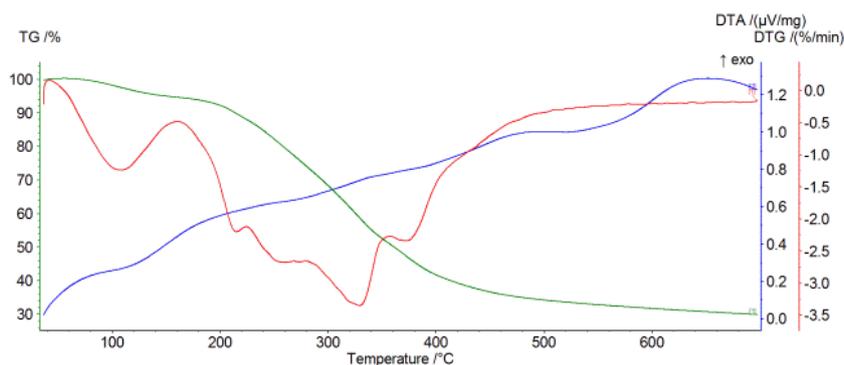

Figure 3. SEM-EDS spectra of biomass samples: A) straw waste, B) rape residue

A) straw waste

B) rape residue

Figure 4. Thermal analysis of biomass samples: A) straw waste, B) rape residue

Figure 3 illustrates the SEM-EDS spectra for the biomass samples. The SEM images showed the porous morphology of compared to the woody and fibrous surface structure. SEM also shows that straw is a porous material and appears that after modification, the surface structure could be smoother. In addition small beads on biomass samples are eliminated, which was ascribed to the reduction of most lignin, hemicellulose and other impurities The EDS spectra of biomass waste showed the occurrence of several alkali metal aggregates such as K, Ca and Mg. The combustion processes biomass waste (Fig. 4) could be divided into three stages, including dehydration of moisture (Stage I), releases of volatiles (Stage II) and combustions of char (Stage III) (Limayem and Ricke, 2012). The evolution of Stage I between 80 and 150 °C was attributed to the hydration of moisture. The weight loss and maximum weight loss rate for both straw waste and rape residue in Stage I were higher, which was consistent with the moisture content of the selected samples. For biomass samples, two main stages were found in combustion processes. The first stage was contributed by the devolatilization of the feedstock and volatile combustion up to approximately 400°C. The major weigh loss in this stage was mainly attributed to the decomposition of hemicellulose (220–315 °C), cellulose (315–400 °C) and part of lignin (137–900 °C) and resulted in the formation of char. Subsequently, the evolution took place between 430 and 540 °C was regarded as the combustion of char. The different thermal characteristics among the selected biomass samples were corresponded to the variation of organic compounds and lignocellulosic compositions.

3. Conclusion

The combustion of biomass waste could be divided into three stages. One was volatile matter release and combustion, and the other was the combustion of residual volatile matters and fixed carbon. The existence of catalysts could enhance the release of volatile matters for the first stage, which made the ignition and the maximum combustion rate of biomass waste happen at lower temperatures than that without catalysts.

References

Cai J., Alimujiang, S., (2009), Kinetic Analysis of Wheat Straw Oxidative Pyrolysis Using Thermogravimetric Analysis: Statistical Description and Isoconversional Kinetic Analysis, *Industrial & Engineering Chemistry Research*, **48 (2),** 619–624.

Demirbas A. (2005), Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues, *Progress in Energy and Combustion Science*, **31 (2)**, 171–192.

Demirbas A. (2004), Combustion characteristics of different biomass fuels. *Progress in Energy and Combustion Science*, **30 (2)**, 219–230.

Gierlinger N., Goswami L., Schmidt M., Burgert I., Coutand C., Rogge T., *et al.*(2008), In situ FT-IR microscopic 414 study on enzymatic treatment of poplar wood cross-sections, *Biomacromolecules,* **9 (8),** 2194-2201.

Idris S.S., Rahman N.A., Ismail K., (2012). Combustion characteristics of Malaysian oil palm biomass, sub-bituminous coal and their respective blends via thermogravimetric analysis (TGA), *Bioresource Technology*, **123**, 581–591.

Kristensen J.B., Thygesen L.G., Felby C., Jørgensen H., Elder T. (2008) Cell-wall structural changes in wheat straw pretreated for bioethanol production, *Biotechnology for Biofuels,,*
https://biotechnologyforbiofuels.biomedcentral.com/articles/10.1186/1754-6834-1-5

Limayem A., Riske S.C. (2012), Lignocellulosic biomass for bioethanol production: current perspectives, potential issues and future prospects, *Progress in Energy and Combustion Science*, **38 (4)**, 449-467.

Lee J.W., Hawkins B., Day, D.M., Reicosky D.C (2010), Sustainability: the capacity of smokeless biomass pyrolysis for energy production, global carbon capture and sequestration, *Energy & Environmental Science,* **3 (11)**, 1695–1705.

Mushtaq F., Mat R., Ani F. N. (2014), A review on microwave assisted pyrolysis of coal and biomass for fuel production, *Renewable and Sustainable Energy Reviews,* **39**, 555-574.

Părpăriță E., Nistor M.T., Popescu M.-C., Vasile C. (2014), TG/FT – IR/MS study on thermal decomposition of polypropylene/biomass composites, *Polymer Degradation and Stability*, **109**, 13-20.

Piriou B., Vaitilingom G., Veyssiere B., Cuq B., Rouau X. (2013), Potential direct use of solid biomass in internal combustion engines, *Progress in Energy and Combustion Science,* **39 (1)**, 169–188.

Sanders J.P.M., Clark J.H., Harmsen G.J., Heeres H.J., Heijnen J.J., Kersten S.R.A., van Swaaij W.P.M., Moulijn J.A. (2012), Process intensification in the future production of base chemicals from biomass, *Chemical Engineering and Processing,* **51**, 117-136.

Sikarwar V.S., Zhao M., Clough, P., Yao J., Zhong X., Memon M.Y., Shah N., Anthony E.J., Fennell P.S. (2016), An overview of advances in biomass gasification, *Energy & Environmental Science*, **9**, 2939-2977.

Varol M., Atimtay A.T., Bay B., Olgun H. (2010), Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis, *Thermochimica Acta*, **510**, 195-201.

Verma M., Godbout S., Brar S.K., Solomatnikova O., Lemay S.P., Larouche J.P. (2012), Biofuels production from biomass by thermochemical conversion technologies, *International Journal of Chemical Engineering,* **2012**, 18 pages.

Yang S.I., Wu M.S., Wu C.Y. (2014), Application of biomass fast pyrolysis part I: Pyrolysis characteristics and products, *Energy*, **66**, 162-171.

Zhang K.H., Zhang K., Cao Y., Pan W.P. (2013), Co-combustion characteristics and blending optimization of tobacco stem and high-sulfur bituminous coal based on thermogravimetric and mass spectrometry analyses, *Bioresource Technoogy*, **131**, 325–332.

Zhou Ch., Liu G., Wang X., Qi C. (2016), Co-combustion of bituminous coal and biomass fuel blends: Thermochemical characterization, potencial utilization an environmental advantage, *Bioresource Technology*, **218**, 418-427.

Zhou C.C, Liu G.J., Fang T, Lam P.K.S. (2015), Investigation on thermal and trace element characteristics during co-combustion biomass with coal gangue, *Bioresouce Technology*, **175**, 454–462.