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4 authors:

Simona Domazetovska
Ss. Cyril and Methodius University

Vladimir Strezov
Macquarie University

Tao Kan
Macquarie University

Risto V. Filkoski
Ss. Cyril and Methodius University

Thermal behaviour of different biomass materials under slow pyrolysis conditions

Simona Domazetovska[1,2*], Vladimir Strezov[2], Tao Kan[2], Risto Filkoski[1]

[1]Faculty of Mechanical Engineering, University "Ss Cyril and Methodius, Skopje, R. Macedonia;
[2]Department f Environmental Sciences, Faculty of Science and Engineering, Macquarie University, NSW 2109, Australia

[*]corresponding author e-mail: simona.domazetovska@hotmail.com

Extended Abstract

The use of carbon neutral renewable sources to achieve reduction in carbon emission, soaring prices of petroleum and concerns over secured supply of energy sources are the major drivers in the search for alternative renewable energy sources. Typical and abundant biomass residues, such as corn cob, vine rod and sunflower have potential to produce energy when subjected to pyrolysis conversion through biogas, bio-oils and bio-char products of pyrolysis.

The subject of investigation of this work was to determine the thermal behaviour of these three biomass agricultural materials under slow pyrolysis conditions to quantify their energy content. In this work, a variety of technological tools were employed to characterise the pyrolysis of the three samples. The thermo-gravimetric analyser and proximate analyses were used on the raw samples to monitor the mass change and characterise the samples. The organic compounds contained in the pyrolysis oils at 500˚C were investigated using gas chromatography- mass spectrometry (GC-MS). The solid char products of pyrolysis at 500˚C and the raw samples were analysed using Fourier transform-infrared (FT-IR) spectroscopy.

The results indicate change in functional groups between raw and solid char products, which refers to the loss of organics after pyrolysis at 500˚C. The composition in the bio-oil was compared of the selected biomass materials. Through proximate analysis, the calorific value was determined.

The obtained data will provide important reference information for energy and fuel generation from pyrolysis of the analysed biomass.

Introduction

The use of renewable energy sources is becoming increasingly necessary, if we are to achieve the changes required to address the impacts of global warming. Biomass is the most common form of renewable energy, widely used in the third world but until recently, less so in the Western world [1]. With the rapid increase in global energy demanding and increasing environmental and sustainability challenges, biomass fuels as renewable energy sources have increasingly been considered as one of the key options to substitute conventional fossil fuels. Currently, biomass and waste contribute to around 10% of the global energy supply [2]. Pyrolysis is one of the thermochemical technologies for converting biomass into energy and chemical products consisting of liquid bio-oil, solid biochar and pyrolytic gas

[3]. Bio-oil is a complex mixture, highly oxygenated with a great number of large size molecules, which nearly involve all species of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids and alcohols [4]. L. Van Zwietren et al., in their work expect that bio-oil is thought to play a dominant role as a substitute for the crude oil due to its significant potential for the production od energy through direct combustion [5]. Bio-oil can be further upgraded for a better quality to make it suitable for engine applications [6]. Biochar is a porous carbonaceous solid product of pyrolysis or incomplete combustion of organic materials, similar to charcoal but also utilized for agricultural and biological activities and/or environmental applications [7]. Furthermore, bio-char has the potential to be used as a soil amendment due to its very high surface area, which improves the water holding capacity of the soils, has nutritient dynamics and supresses nutrient leaching [8]. As a mixture of a volatile gases, which consist primarly of CO_2, CO, CH_4 and higher hydrocarbon compounds, pyrolitic biogas can also be used as a combustible fuel [9]. Grapes are one of the world's largest fruit crops and grape stalks are one of the wastes generated by grape juice and wine-making processes. They are currently disposed of by distilleries, land fill or in rural areas [10]. Investigating the potential of corn residues for energy, fuel, materials and chemicals production according to their thermochemical treatment products yields and quality, it can be stated that corn cob could be a solid and gaseous biofuel and they could be a good material for activated carbon production after being activated or gasified with steam [11]. Sunflower is a traditional crop which can be used for the production of bioenergy and liquid biofuels [12].

Methodology

Biomass residues: corn cob, vine rod and sunflower were collected and investigated with experimental techniques, such as thermogravimetric analysis, Fourier spectroscopy, gas chromatography and gas chromatography-mass spectroscopy.

Mass change of samples during pyrolysis - Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed with thermogravimetric analyser TGA/DSC 1 STARe System, Mettler Toledo Ltd. It was measured the mass loss of the samples (corn cob, vine rod and sunflower) during heating from 25℃ to 1000℃ under a heating rate od 10℃/min, with nitrogen as carrier gas at flow rate 20 ml/min. A differential thermogravimetric curve was obtained by differentiating the thermogravimetric curve.

Proximate analysis

It was used the instrument TGA/DSC to achieve proximate analysis on the analyzied samples: corn cob, vine rod and sunflower. It is analyzied the percentage of the: moisture, volatile matter, ash and fixed carbon.

Characterisation of products from pyrolysis

An infrared furnace with temperature-programming was used to extract gaseous (pyrolytic gas), liquid (mainly pyrolysis oils) and solid matter (chars) by pyrolysis of corn cob, vine rod and sunflower. The fine particles of each rubber type were packed in a quartz tube fixed-bed reactor at a heating rate of 10 ºC/min in an inert helium atmosphere.

Fourier Transform Infrared Spectroscopy (FT-IR)

The raw samples of corn cob, vine rod and sunflower were heated to 500℃ for char production. Fourier transform infrared (FT-IR) spectrometer (model: Nicolet 6700 FT-IR) with an attenuated total reflectance (ATR) was used to acquire the functional groups of the raw samples and the chars after pyrolysis. The total number of scans was 32, with a spectral resolution of 4 cm^{-1}.

Gas Analysis (GC)

Pyrolitic gas was released and analysed during the pyrolysis process, carried out from room temperature to 800℃ by an online micro gas chromatograph (model: M200, MTI Analytical Instruments). There were two thermal conductivity detectors, and an ultra-high purity helium as a carrier gas, used in the analysis. The hydrogen and carbon monoxide peaks were determined by molecular sieve 5A column at 60℃ with carbon dioxide, methane, ethane and ethylene.

Gas chromatography- mass spectroscopy (GC-MS) analysis

The pyrolysis oils were continuously swept out of the reactor exit until the temperature reached 500℃. The quartz wool was washed using dichloromethane (DCM) to extract the pyrolysis oil components which were derivatised by N,O- bis (trimethylsilyl) trifuoroacetamide with 1% trimethylchlorosilane (BSTFA+1%TMCS). The model that was used to test the detailed components of pyrolysis oils is: Agilent 7890B GC with 5977A MS system equipped with a HP-5MS column (60m x 0.25 μm). The oven was initially set to 40℃ for 2 minutes, then heated to 310℃ at 2℃$/min$ and kept at 310 ℃ for 30 minutes.

Results

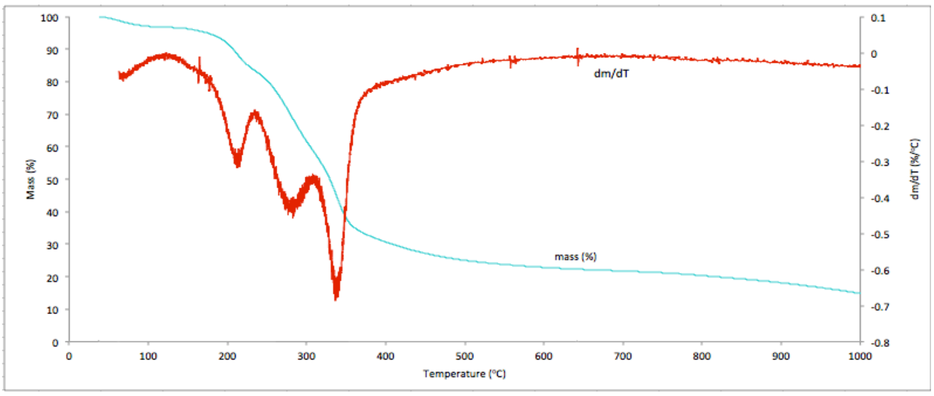
The results of the proximate analysis of biomass waste: corn cob, vine rod and sunflower, obtained with TGA/DSC instrument, are presented in Table 1.

Table 1. Proximate analyses of corn cob, vine rod and sunflower

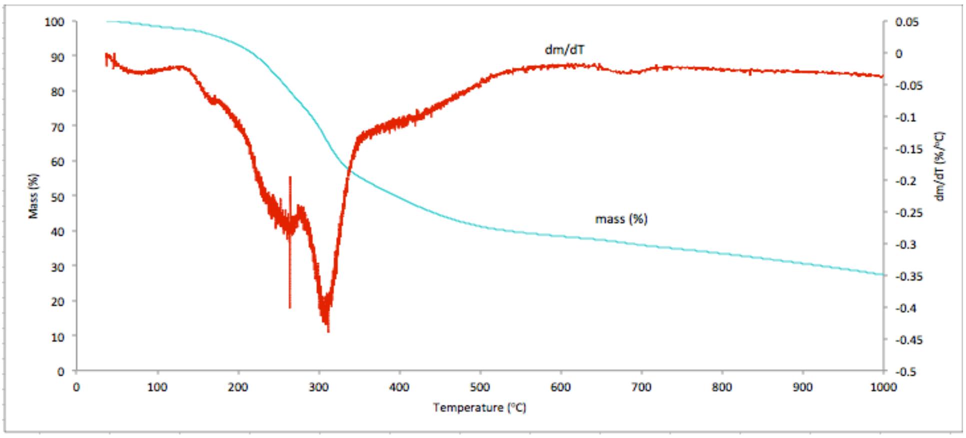
Sample name	Moisture content (%)	Volatile matter content(%)	Ash content (%)	Fixed carbon (%)
Corn cob	2.77	80.18	1.73	15.33
Vine rod	3.90	69.33	4.06	22.71
Sunflower	2.94	72.05	8.30	16.71

As a result of the three analysed samples, it was found that the corn cob has highest percentage of volatile matter content (80.18%), but has the lowest ash content (1.73%). The vine rod was found to have the highest moisture content (3.90%) of all three examined samples, and high content of fixed carbon (22.71%). All of the three samples were found to have high volatile matter and fixed carbon content, i.e. 90% of all contents.

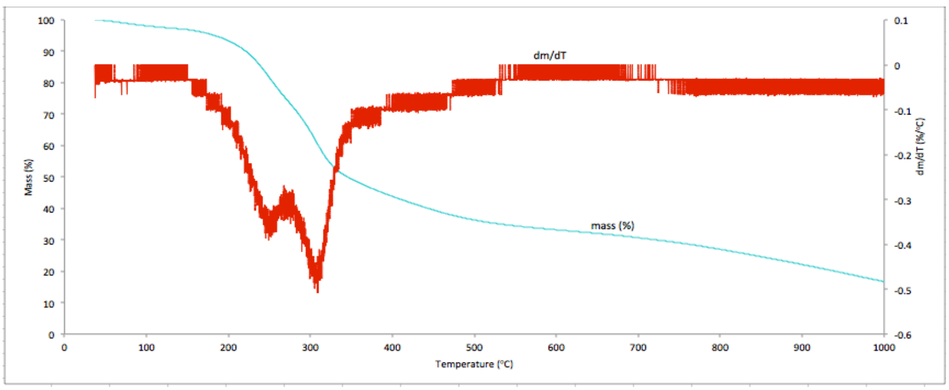
The mass change of the samples during pyrolysis in function of the temperature, as determined by the Thermogravimetric Analysis method is shown in Figure 1.



(a)



(b)



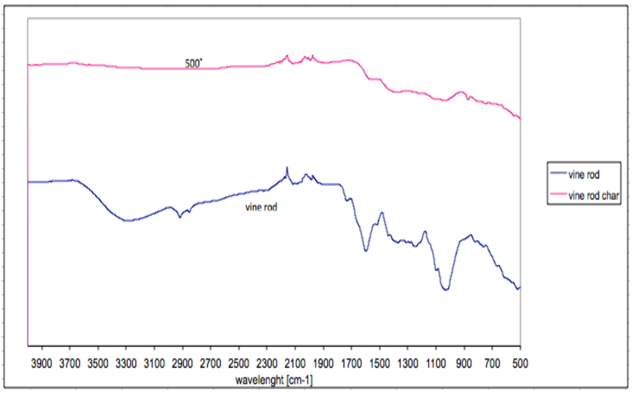
(c)

Figure 1. Thermogravimetric analysis of (a) corn cob; (b) vine rod; (c) sunflower

In Figure 1, it is shown the mass loss during increasing the temperature of the samples from room temperature to 1000℃ with heating rate 10℃/min. On DTG (Differential Thermogravimetric) curve is shown the specific heat change in function of the temperature, i.e. the percentage change of the mass in function of temperature (%/℃). From the three examined samples, it is found that the biggest degradation of the mass happens from 200℃ to 450℃, which shows the degradation of organic matters. At 500℃, the biggest degradation has the corn cob with mass content of 24%, then sunflower with 36% and the vine rod with 40% of mass content.

Figure 2 shows the Fourier Transform Infrared (FT-IR) spectroscopic data of the biomass waste and its char products. The solid products of pyrolysis, were produced at temperature at 500℃ . The FTIR spectra of the corn cob on figure 2(a) shows that the greatest changes happen from 500 cm^{-1} to 1750 cm^{-1}, which are expressed with much lower intensity at the bio-char. After 1750 cm^{-1}, the change of the bio-char is unremarkable, which shows that it is fully decomposed. Compared to raw corn cob, bio-char loses the functional groups O-H and >CH_2. From Figure 2(b), it is found that the greatest changes happen from 500 cm^{-1} to 1800 cm^{-1} wavelenght. Compared to raw vine rod, bio-char loses the functional groups O-H and >CH_2. From Figure 2(c), it is found that the bio-char from the sunflower has less functional groups and changes because of the loss of organic compounds. In comparasion with the raw sunflower, bio-char is fully decomposed.

(a)



(b)

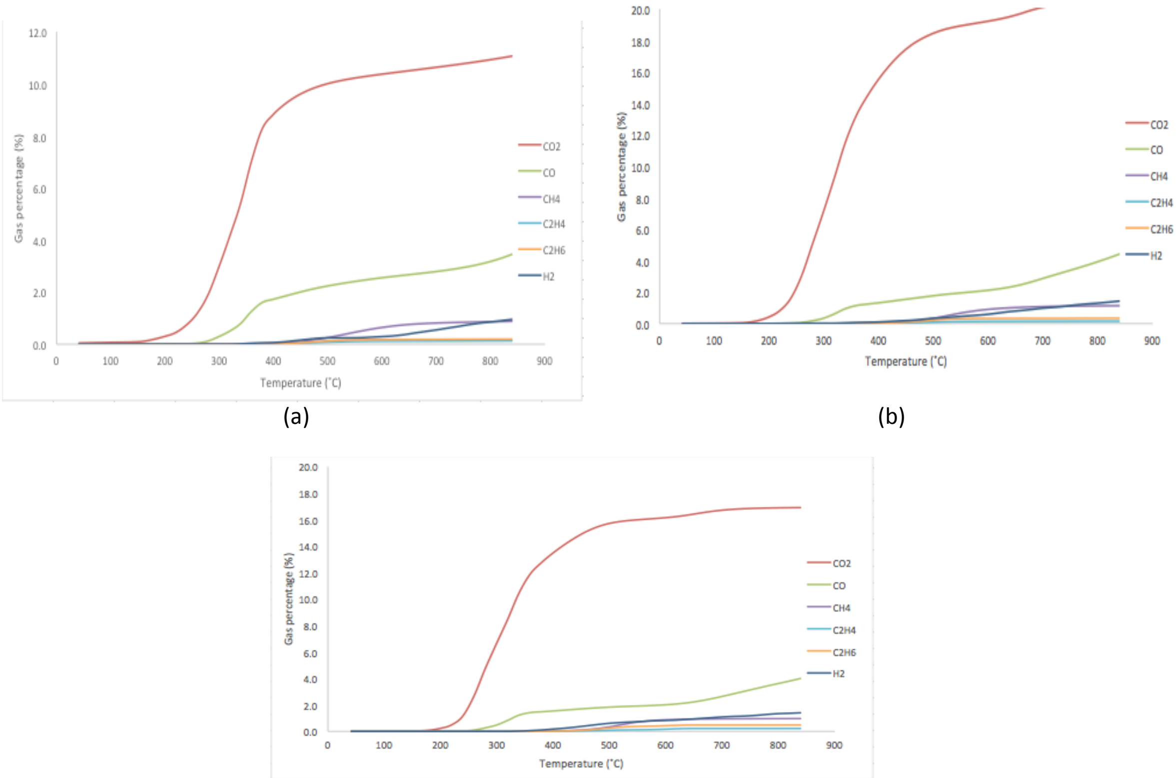
(c)

Figure 2. FTIR spectra of biomass waste pyrolysis products; (a) corn cob; (b) vine rod; (c) sunflower

The gas evolution rates of the major volatile products of biomass waste are shown in Figure 3. The percentage amount of gases from corn cob released during the temperature rise is shown in Figure 3(a). At 500°C, of the total amount of biomass from corn cob, 12.92% are gases, out of which 10% is CO_2, 2.23% is CO, 0.25% CH_4, 0.24% H_2 and the other gases participate with smaller amount.

In Figure 3(b) it is shown the percentage amount of gases from the vine rod during the temperature rise, which shows that at 500°C 21.18% of the whole mass of the sample has been released as gaseous matter. From the whole amount of gases, CO_2 contributes with largest amount, 18.44%, followed by CO with 1.76%, H_2 with 0.33%, CH_4 with 0.32% and the other gases with smaller percentage.

In Figure 3(c) is shown the amount of gases from sunflower released during the heating. At 500°C, of the total amount of biomass from sunflower, 18.82 % are gases, of which 15.7% is CO_2, 1.83% is CO, 0.34% CH_4, 0.61% H_2 and the other gases with smaller amount.



(a) (b)

(c)

Figure 3. Percentage amount of gases of biomass waste pyrolysis (a) corn cob; (b) vine rod; (c) sunflower

From the results of the gas chromatography - mass spectrometry analysis, it is found that the most common are the compounds that contain oxygen. These bio-oils have potential for further use. Because of the high quantity of acids, it is recommended that hydrothermal process should be used to reduce the amount of oxygen.

Conclusion

Biomass residues are potential source of energy locally. In this study, three different biomass types, including corn cob, vine rod and sunflower, were pyrolysed at $10^{o}C$/min to generate fuel of pyrolytic gas, oil and char. The process of pyrolysis is one of the options that offer conversion of the biomass waste to higher value products, such as bio-oils, bio-gas and bio-char. From the proximate analysis of the considered biomass types, it can be concluded that they are the best to use for production of gaseous bio-fuel. The fixed carbon as the second most abundant content, can be used to improve the properties of soil. The oxides of carbon, CO_2 and CO , as well as H_2 and CH_4 were basically the primary gas species in the gas product, indicating the potential of using the pyrolytic gas. In terms of bio-oil analysis, chemical compounds with their relevant contents were identified [9]. Palmitic acids and catechol were the dominant compounds in the bio-oils, indicating its great potential for further biodiesel production . Generally, biomass pyrolysis is currently at the mature stage of development with several technologies already achieving full commercialization stage. Their input into the global energy production is expected to achieve the full potential in the near future [13].

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