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Products characterization study of a slow pyrolysis of biomass-plastic mixtures in a fixed-bed reactor

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ABSTRACT

In this study, *co*-pyrolysis of plastic wastes; polyvinyl chloride (PVC) and polyethylene terephthalate (PET) with different agricultural wastes such as cotton stalk, hazelnut shells, and sunflower residues near an arid land plant *Euphorbia rigida* was investigated. Thermal behaviors of raw materials were investigated by using thermogravimetric analyzer. Experiments were conducted at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in the presence of N_2 atmosphere with a flow rate of 100 cm^3 min^{-1}. In the light of the experimental results, an appropriate temperature for the fixed-bed pyrolysis of biomass-plastic mixtures at (1/1, w/w) was determined and the raw materials were pyrolyzed at the same conditions except until the final temperature of 500 °C. Solid product (char) and liquid product (tar) of the pyrolysis were characterized by using different types of characterization techniques. Pyrolysis experiments showed that mixing by biomass and plastic materials had a positive effect on the liquid and gas yields. In addition, the characterization studies showed that biomass and plastic materials could be used to convert into valuable chemicals.

1. Introduction

The energy requirement is accelerating drastically when the population growth and the increase in the technological developments come across with the changing consumption habits of modern society. As a result, the present rate of economic growth is unsustainable without saving of fossil energy like crude oil, natural gas or coal. On the other hand, suitable waste management strategy is another important aspect of sustainable development, since most of the materials such as plastics used in daily life are based on petrochemical origin. In addition to their chemical and physical resistance and low costs, plastic materials increasingly take an active role in both daily and industrial activities due to their ease of production facilities. Plastics are used in a number of implementations from greenhouses to coating, wiring, packaging, films, covers, bags and containers. Every day, great numbers of plastic wastes are being generated by the individual and democratic production and consumption. Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins. These groups have different roles and are subjected to different management strategies [1–4]. Significant features and the wide range application areas generate another problem in terms of removal process of plastic materials. Traditional disposal methods such as landfilling and incineration are not appropriate for every type of plastic waste and may create unpredictable dangers for the environment [5]. At this point, new and alternative techniques take an active role via today's technology. In the literature, four possible methods that can be classified as clean technologies which are: waste-to-energy; composting and anaerobic digestion; pyrolysis and gasification; and material recycling come to the fore [6].

Although, Turkey has limited fossil sources, due to its geographical location, the agricultural sector has been Turkey's largest employer and a major contributor. In fact, this situation results in large agricultural potential which can be evaluated as biomass sources. That is why biomass energy should come forward among other alternative energy sources [7]. Turkey has a capacity to stand at the top ten for the production of different and generous agricultural products in the world due to its various climates in different geological regions. One of these agricultural products is sunflower. Turkey is an ideal country for growing sunflower and an important producer along with Russia, the USA, India, Argentina and China

Abbreviations: CS, cotton stalk; HS, hazelnut shell; SFR, sunflower residue; ER, Euphorbia rigida; PP, polypropylene; PS, polystyrene; PE, polyethylene; PET, polyethylene terephthalate; PVC, polyvinyl chloride; TGA, thermogravimetric analyzer; DTG, differential thermogravimetric analysis; FT-IR, Fourier transform infrared spectrometer; GC–MS, gas chromatography–mass spectrometry.

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[8]. On the other hand, the country still protects its first place in the world hazelnut production. Annual hazelnut production of Turkey is approximately 500 000 t and half of this is shell as by-product [9]. In addition, Turkey is one of the eight countries producing 85% of the world's cotton. Cotton is being cultivated mainly for its lint, which is universally used as a textile raw material. However, cotton stalk constitutes a big potential as a by-product of textile industry without any feasible evaluation [10]. Besides all these agricultural and industrial biomass feed stocks, the country also has important energy plants which can be classified as non-edible. *Euphorbia rigida* is an arid-land plant which contains an important amount of latex compound and can be converted into valuable chemicals via different thermochemical conversion techniques [11].

Utilization of biomass-plastic mixtures with *co*-processing technologies such as *co*-combustion [12], *co*-liquefaction [4], *co*-pyrolysis [13] or *co*-briquetting [14] has become very popular in recent years. The fundamental goal of *co*-processing technologies is to make environmental degradation easier while maintaining productivity and profitability. It is therefore important to determine the efficiency levels of input use for agricultural residues and plastic wastes [15]. Particularly, biomass has a considerable place for *co*-pyrolysis applications to assess with plastics for producing various chemicals and fuels. There are numbers of studies about the *co*-pyrolysis of biomass-plastic wastes. Most of these studies contains experimental data about *co*-pyrolytic behaviors of polyolefines such as polyethylene (PE), polypropylene (PP), polystyrene (PS) with biomass materials. Pine wood-PP [16], wood sawdust-PP [17], rubber seed shell-HDPE [18], wood pellets-PE [19], olive residue-LDPE [20], hazelnut shell-PE [9], pine cone-PE/PP/PS [21], apricot timber-PE/PP/PS [22] are some of the important examples in the literature. Uzun et al. emphasized that data obtained from these studies demonstrated that the *co*-pyrolysis of plastic and biomass resulted in a high oil yield with an acceptable quality [23]. During the thermal degradation, polyolefines act as H_2 donor and lead hydrogen transferring from a polyolefinic chain to biomass-derived radicals [24]. However, *co*-pyrolysis mechanism of biomass-plastic mixtures is not still very clear and depends on the type of the changing feedstock. In order to create additional data for the *co*-pyrolysis of biomass-plastic mixtures, other widely used plastic materials such as polyethylene terephthalate (PET) from daily activities and polyvinyl chloride (PVC) from industrial activities were preferred as polymer precursors. Even though PET has wide range of application areas in industry, such as prepaid cards, films, fibers and tapes, it still protects its first place as a most encountered plastic material in daily life [25]. On the other hand, polyvinyl chloride (PVC) situates behind polyethylene in the second rank as an important industrial plastic around the world. PVC is mostly used in construction, wiring, transportation etc. As a result of that consumption, PVC waste amount is increasing drastically [26] and the destruction of these kinds of wastes is becoming more prevalent. It was believed that the structural differences of these plastics may directly affect the product yield and composition during the pyrolysis. Another additional value of the present study is not only the types of the plastic materials but also justifying the selection of the fuel/waste, based on the local availabilities. All biomass samples has their own importance according to geographical region they grow up, their structural differences and the part of plant (shell, stalk, whole body etc.) used in the experiments. With the above considerations, cotton stalk, hazelnut shells, sunflower residues besides *E. rigida* were blended in definite ratio (1/1, w/w) and pyrolyzed with polyvinyl chloride (PVC) and polyethylene terephthalate (PET) in fixed bed reactor after the determination of the appropriate temperature for the fixed-bed experiments. Pyrolysis products were characterized by using different characterization techniques. Experimental results showed that biomass and plastic materials could be transformed into valuable chemicals by using pyrolysis which is one of the most important thermochemical conversion techniques.

Table 1
Proximate and component analysis of biomass materials (wt.%).

	CS	HS	SFR	ER
Proximate Analysis (as recieved)				
Moisture	7.46	10.94	6.05	3.02
Ash	5.52	0.71	9.34	6.72
Volatiles	64.92	68.98	65.26	75.05
Fixed C*	22.10	19.36	19.35	15.21
Component analysis (dry basis)				
Holocellulose	72.75	72.61	65.45	48.67
Oil	6.80	5.01	4.25	5.15
Extractive	5.63	5.36	14.04	12.55
Hemicellulose	21.68	25.48	35.18	29.50
Lignin	22.16	23.46	20.94	37.92

* Calculated by difference.

2. Experimental procedure

2.1. Materials

In the present paper, four types of biomass; cotton stalks (CS), hazelnut shells (HS), sunflower residues (SFR) and *E. rigida* (ER) were preferred [8]. The raw materials were provided from different geographical regions of the country. Cotton stalk and *E. rigida* are from Mediterranean gegion, hazelnut shells are from Black Sea Region, and sunflower residues are from Marmara Region. The other feedstock materials were chosen as plastic wastes from daily and industrial activities which are polyethylene terephthalate (PET) and polyvinyl chloride (PVC). Used water bottles were collected as PET source while PVC samples were obtained from a local plant. Before the experiments, biomass materials were prepared for the proximate and component analyses by washing with distilled water, air drying and milling in a high speed rotary cutting mill. The average particle size was determined between 0.425 and 1.25 mm.

2.2. Characterization of raw materials

Before thermochemical conversion of raw materials, some characterization studies were carried out for biomass samples. Proximate and component analyses were carried out for all biomass materials according to the ASTM procedure and the results were given in Table 1. The functional groups in the structure were determined by using FT-IR (Bruker Tensor 27 Model Fourier Transform Infrared Spectrometer) by using dried KBr technique. In this method, dried KBr and raw samples were mixed in the weight percentage of 99–1% and these mixtures were used to prepare pellets. For the determination of the surface characteristics, scanning electronic microscope (SEM) Jeol Camscan was used. Samples were mounted on an aluminum stub using carbon bands and coated with a thin layer of gold-palladium in an argon atmosphere using Agar Sputter Coater.

2.3. Determination of the thermal characteristics of the materials

In the previous study [8], all raw materials were pyrolyzed in a thermogravimetric analyzer (TGA) in order to determine the thermal behaviors. A SETERAM-LABSYS evo thermogravimetric analyzer was used during the experiments. About 5–15 mg of sample was pyrolyzed under 100 $cm^3\,min^{-1}$ N_2 flow at heating rate of 10 °C min^{-1} from room temperature to 800 °C. Thermal behavior curves of the materials were given in Fig. 3.