



Insights into pyrolysis and co-pyrolysis of biomass and polystyrene: Thermochemical behaviors, kinetics and evolved gas analysis

Gamzenur Özsin*, Ayşe Eren Pütün

Anadolu University, Department of Chemical Engineering, Faculty of Engineering, Eskişehir 26555, Turkey



ARTICLE INFO

Keywords:
Biomass
Polystyrene
Pyrolysis
TGA/MS/FT-IR
Kinetic
Gas analysis

ABSTRACT

The purpose of this study was to investigate the effect on polystyrene (PS) during co-pyrolysis with biomass through thermal decomposition. The model-free iso-conversional methods (Kissinger, Friedman, Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose, Starink and Vyazovkin) were adopted to calculate activation energy of the pyrolysis and co-pyrolysis process of two biomass samples (walnut shell: WS and peach stones: PST) with PS. It is found that biomass blending to PS decreased activation energy values and resulted in multi-step reaction mechanisms. Furthermore, changes in the evolution profiles of methyl, water, methoxy, carbon dioxide, benzene and styrene was monitored through evolved gas analysis via TGA/FT-IR and TGA/MS. Detection of temperature dependent release of volatiles indicated the differences occur as a result of compositional differences of biomass.

1. Introduction

Rapid industrialization and massive population growth has caused a dramatic increase in municipal solid waste (MSW) throughout the world. On the other hand, high demand for energy, irregular distribution of fossil fuel sources together in politically unstable regions with concerns over global climate change has attracted attention to use of waste as an energy producer [23,24,22,15]. Eliminating MSW while gaining energy recovery has been one of the most debated issues for several decades [54]. For this purpose, thermochemical processes have drawn attention as they represent an interesting option for utilization of waste materials such as plastics, biomass, and industrial or municipal sludge [59,29,17,12,9,11,42,30]. One of the thermochemical conversion methods, pyrolysis, provides various operational, environmental and economic advantages when it comes to obtaining petroleum substitute liquid fuel, value-added chemicals and char. This process is known as thermo-chemical degradation where an organic material is converted into carbon-rich solid and condensable and non-condensable volatiles by heating in the absence of an oxygen/trace-oxygen atmosphere [32,37,27]. The composition of the product at the end of pyrolysis is dependent on the operating conditions such as temperature, pressure, heating rate, residence time, reactor medium and configuration together with the characteristics of the raw material [8,26,7]. The production of fuels and chemicals has been addressed following two main strategies; the development of specific pyrolysis processes and the integration of waste-derived products in refinery units [31].

From the sustainability point of view, it is better to utilize different

wastes at the same time during pyrolysis. Nowadays, co-pyrolysis technique is regarded as one of the most promising methods. Because it enhances yield of petrochemicals, improves the selectivity of desired compounds, and reduces the coke formation through synergetic effects [60,7,1]. Especially, several studies have shown that co-pyrolysis technique offers several advantages when it was applied to biomass and plastics. Because, when biomass is pyrolyzed alone, the produced liquid products are mostly unstable and oxygenated. Due to detrimental properties of bio-oils such as low heating value, high acidity, high viscosity, and high reactivity they cannot be directly used. Hence, they should be upgraded prior to use. On the other hand, synergy may be created during co-pyrolysis of biomass and polymers because of the high hydrogen contents of the polymers during degradation [38,57,36,62,60].

For designing, optimization, and scaling up to industrial plant level, a real understanding of pyrolysis kinetics is required to achieve the best energy recovery. However kinetic modeling of pyrolysis and co-pyrolysis processes is a challenging task since the exact reaction mechanism which includes series of exothermic and endothermic reactions and the effects that the feedstock composition creates in product yields are still not well understood [47,41,46,53]. In pyrolysis, the primary steps of thermal decomposition followed by secondary reactions (cracking, gas phase/char interactions, etc.) occur and all these processes are often in competition with heat and mass transfer phenomena [28]. To this end, thermogravimetric analysis (TGA) coupled with spectroscopic methods is the most widely used technique when it comes to obtaining information about thermal decomposition process, and in

* Corresponding author.

E-mail address: gozsin@anadolu.edu.tr (G. Özsin).

interpretation of pyrolysis kinetics and simulate chemicals or evolved species.

In this study, pyrolysis and co-pyrolysis of two biomass samples (walnut shell; WS and peach stones; PST) with polystyrene (PS) were investigated by employing the combination of TGA, MS and FT-IR techniques. The target polymer was selected as PS, since it is known to create synergetic effects that improve the properties and the yield of pyrolytic oil [45,21]. Prior to this presented study, co-pyrolysis of several biomass samples with PS were carried out by using conventional pyrolysis reactors and researches were mainly focused on to investigate the properties of the liquid and solid products. The novelty of the presented paper is due to the fact that biomass samples together with PS have never been tested in a TGA/MS/FT-IR system through co-pyrolytic degradation. Within the scope of the study, thermochemical behaviors and interactions during pyrolysis and co-pyrolysis were clarified with the help of the collected data from simultaneous TGA/MS/FT-IR measurements. Model-free iso-conversional methods were adopted for apparent activation energy acquisition and the evolution of gases was simultaneously monitored to deduce the reaction mechanism.

2. Materials and methods

2.1. Experimental study

2.1.1. Preparation and characterization of raw materials

The biomass and PS samples were grounded in to a uniformed particle size. Blends were prepared by mixing samples at a definite ratio of 1:1 (wt. biomass/wt. PS). A particle size between 112 μm and 224 μm was used throughout the thermoanalytical measurements. To conclude efficiency of pyrolysis and interpretation of the characteristics of the product distribution, physical and chemical characteristics of precursors are essential during pre-planning phase. Prior to the TGA/FT-IR/MS experiments, proximate, ultimate and component analyses were performed by using ASTM standards (ASTM E871-82, ASTM ASTM D1102-84, ASTM E872-82, ASTM E870-82, ASTM D1107-96, ASTM D1106-96, ASTM D5373-16). Experiments for proximate analysis were performed on wet basis (as-received basis), whereas elemental and compositional analysis were done and reported as dry-ash free (daf) basis. Primary characteristics of the biomass samples and PS were given in Table 1 as arithmetic mean of three repeated experiments. When the properties of biomass samples were investigated, it can be said that the contents of the volatiles and moisture are slightly higher in WS as 76.45

Table 1
Properties of the raw materials.

| | WS | PST | PS |
|--------------------------------------|--------|--------|--------|
| <i>Proximate analysis (%)</i> | | | |
| Moisture | 6.98 | 6.88 | 0.86 |
| Ash | 0.58 | 0.86 | 0.98 |
| Volatiles | 76.45 | 72.42 | 97.71 |
| Fixed carbon ^a | 15.99 | 19.84 | 0.45 |
| <i>Component analysis (%)</i> | | | |
| Hemicellulose | 26.20 | 25.10 | – |
| Lignin | 36.89 | 39.26 | – |
| Extractives | 4.14 | 5.28 | – |
| Cellulose ^a | 32.19 | 29.50 | – |
| <i>Elemental analysis (%)</i> | | | |
| C (%) | 47.52 | 49.28 | 90.34 |
| H (%) | 6.71 | 6.65 | 9.06 |
| N (%) | 0.21 | 0.34 | 0.29 |
| O ^a (%) | 45.56 | 43.73 | 0.31 |
| H/C | 1.683 | 1.609 | 1.196 |
| O/C | 0.720 | 0.666 | 0.003 |
| Calorific value (MJ/kg) ^b | 17.836 | 18.379 | 43.576 |

^a From difference.

^b From Dulong's equation.

and 6.98 wt%, respectively. From the biochemical composition perspective, high lignin contents of both samples were noticeable. The highest lignin content was found in the PST, i.e. 39.26 wt% while it was 36.89 wt% in the WS structure. It is known that lignin provides a natural resistance to thermal degradation, however it contributes to bio-fuel having a substantially higher heating value [52]. Even though the proximate and component analysis indicated key differences between the biomass samples, an elemental analysis was performed in order to show the actual differences of biomass samples and PS. Accordingly, highest carbon (90.34 wt%) and hydrogen (9.06 wt%) and hence lowest H/C (1.196) and O/C (0.003) ratios were obtained in PS, as expected. The calorific values of the WS and PST together with PS have been reported in the proximate analysis and the heating value of PS (43.6 MJ/kg) was found to be higher than in WS (17.5 MJ/kg) and PST (18.4 MJ/kg) due to higher elemental carbon and hydrogen content of PS.

Other than proximate, ultimate and component analysis, the quantity of ash and its elements also affect thermal degradation characteristics of biomass and product yield. Hence, inorganic constituents of the biomass samples were determined using XRF technique (by Rigaku XRF, ZSX). The results regarding the mineralogy of the biomass ashes are summarized in Table 2. Results showed that K₂O is the main contributor to the ash composition for both two biomass samples.

2.1.2. Thermoanalytical measurements

The thermoanalytical measurements were carried out under an inert atmosphere using a TGA device (Setaram-Labsys Evo) coupled to a FT-IR spectrometer (Thermo Scientific iz10) and a mass spectrometer (Pfeiffer Omni Star). Approximately 10 mg of sample was loaded into the Al₂O₃ crucible to prevent possible temperature gradient in the sample and ensure the kinetic control in the process. Before the runs, the Biot number was calculated and found smaller than unity which shows that uniform temperature distribution inside the particle is ensured. Kinetic experiments were performed using linear heating rates from 5 to 40 °C/min and results were monitored from 25 °C to 1000 °C. Both transfer lines to MS and FT-IR detector were heated at 225 °C to prevent condensation of volatiles and dissociate all complexes. During experiments, a continuous nitrogen flow was supplied and its flow rate was maintained at 20 cm³/min. All experiments were performed in triplicates. Detailed explanation of the experimental set-up can be found in our previous study [40].

The evolved gaseous species from the TGA furnace were detected by connecting MS and FT-IR to TGA. FT-IR analysis was performed with the range of 4000–400 cm⁻¹ and a fast recovery deuterated triglycine sulfate (DTGS) detector was used in the spectrometer. In every 5 seconds, 4 scans at 4 wavenumber resolution, resulting in one spectrum

Table 2
Mineralogical analyses of biomass samples.

| Ash | WS | PST |
|--------------------------------|--------|--------|
| Na ₂ O | 1.830 | 1.604 |
| MgO | 4.240 | 11.872 |
| SiO ₂ | 1.092 | 2.322 |
| Al ₂ O ₃ | – | 0.513 |
| P ₂ O ₅ | 4.886 | 13.562 |
| CaO | 39.254 | 18.757 |
| MnO | 0.084 | 0.301 |
| Fe ₂ O ₃ | 0.759 | 7.020 |
| K ₂ O | 43.681 | 40.516 |
| SO ₃ | 3.512 | 3.062 |
| CuO | – | 0.274 |
| ZnO | – | 0.114 |
| SrO | 0.172 | – |
| BaO | 0.364 | – |
| Cl | 0.126 | – |
| Cr ₂ O ₃ | – | 0.083 |

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