



Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene



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ABSTRACT

Biomass from almond shell (aS) was co-pyrolyzed with high density polyethylene (HDPE) polymer to investigate the synergistic effects on the product yields and compositions. The pyrolysis temperature was selected as 500 °C, based on results of TGA-DTG. Co-pyrolysis of HDPE-biomass mixtures were pyrolysed with various proportions such as 1:0, 1:1, 1:2, 2:1 and 0:1. The yield of liquids produced during co-pyrolysis enhanced 23%, as the weight ratio of HDPE in the mixture was doubled. Obtained bio-oils were analyzed with using column chromatography, ¹H NMR, GC/MS, and FT-IR. According to analyses results, produced liquids by co-pyrolysis had higher carbon (26% higher) and hydrogen contents (78% higher), lower oxygen content (%86 less) with a higher heating value (38% higher) than those of biomass oil.

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1. Introduction

Plastics are used in many aspects of human life, but their mass consumption has caused severe environmental pollution, with a great loss of resources from their disposal. Much attention has been paid to solve these problems, with the production of fuel or recycling of valuable chemicals from pyrolysis having been intensively studied as a potential solution. The pyrolysis (or thermal cracking in an inert atmosphere) of waste plastics, particularly polyolefins, arouses great interest for the valorization of these wastes, as it allows high yields of fuels and raw materials to be obtained for the benefit of the petrochemical industry. Moreover, the pyrolysis process has few environmental issues [1,2]. Having a high hydrogen-to-carbon ratios and convenient molecular chain structures, waste commodity plastics such as low and high density polyethylene, polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC) are very suitable for liquid production [3].

Biomass (plant materials) has been recognized as a major world renewable energy source to supplement declining fossil fuel resources. It is composed mainly of cellulose, hemicelluloses, lignin and minor amounts of other organics, which are determined as the elements of carbon, hydrogen and oxygen with high energy content [4]. Biomass energy is destined to play an important role in the future energy systems of the world. Furthermore, it has the advantage of reducing global warming since it uses carbon dioxide through photosynthesis. Biomass could also be sources of energy and raw chemical feedstock because it produces various

biochemical materials. Meanwhile, biomass is typically converted to energy through thermochemical conversion, such as gasification, combustion and pyrolysis. Pyrolysis of biomass has received strong interest in recent decades when the awareness on limited amounts of fossil resources called for alternative solutions based on renewable materials [5]. However, biomass bio-oil has very unstable fuel properties compared with conventional oils. Due to its higher oxygen and acid content; its water content is also too high (over 20 wt.%). Therefore, these shortcomings should be overcome for its use as a regular fuel. To improve the fuel suitability of bio-oil, co-pyrolysis of biomass and organics containing higher hydrogen contents can be considered. Therefore, plastics could potentially be a beneficial feedstock due to their higher hydrogen content and small amount of water in their pyrolysis derived oil. When plastic and biomass are simultaneously pyrolyzed, the stability of the oil product would be expected to be greatly improved compared with that from single biomass pyrolysis, because plastic can provide plenty of hydrogen to the biomass pyrolysis [1].

There are many studies about thermal decomposition of PE, PP, tyre, PS etc. with biomass [5–15]. Data obtained in these studies demonstrated that the co-pyrolysis of plastic and biomass resulted in a high oil yield with an acceptable quality. Nevertheless except for a few studies in the literature, pyrolysis of HDPE with biomass has not been sufficiently investigated [16–18]. For example, Rotliwala and Parikh studied co-pyrolysis of HDPE with de-oiled cake of jatropha (JC) in a batch reactor at 450 °C, under nitrogen flow and at the atmospheric pressure. The yield of liquid product was found to be as 63%. They characterized the liquid phase obtained from co-pyrolysis by gas chromatography–mass spectrometry and ASTM D86 (boiling point distribution) analyses.

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HDPE co-processing with JC significantly increased the proportion of gasoline like (C_6 – C_{12}) fraction to 45% with comparing the HDPE pyrolyzed alone [16] Berruenco et al., studied co-pyrolysis of HDPE/sawdust mixtures in a fluidized bed reactor at five temperatures: 640, 685, 730, 780 and 850 °C. They showed that the gas yield increased and gas composition changed drastically when the temperature was increased for both pure components and the mixture. In addition, average heating value of produced gases by co-pyrolysis of biomass and HDPE are found greater than that of obtained biomass alone [18].

HDPE is the fourth-largest commodity plastic material in the world, after polyvinyl chloride and polypropylene in terms of volume. HDPE has accounted for a major share of ethylene consumption structure over the recent years. The demand for HDPE had an increase of 3.6% in a year to 31.3 million MT in 2011 [19]. In the case of Turkey, according to the Turkish State Statistical Institute's database, 25.28 million tones of municipal waste was collected in 2010 and 33,637 tones of this municipal wastes are plastics. All plastics and other kind of wastes are recovered by methods such as incineration, composting or controlled landfilling [20]. By the way the conversion of waste plastics to valuable chemicals or fuels is more advantageous than the methods mentioned above. Plastics recycling by thermal and chemical methods of conversion of scrap polymers, as gasification, liquefaction, hydrolysis, pyrolysis, and thermo-catalytic degradation, are well known and environmentally accepted. They reduce the impact of waste plastics on the environment and may be a cheap source of energy and useful raw materials [21,22].

Almond is a crop of major importance throughout the world's temperate growing regions with the worldwide almond production in 2011 being approximately 2.00 million ton according to FAO (Food and Agriculture Organization). Turkey is one of the important almond producers among Spain, Greece and Italy in EU. Turkey has a share of 3.5% in the world shelled almond producing and 44,366 tons of almonds and 23,205 tons of almond shells are produced annually. One of the wastes which can be considered to have a good potential as a biomass feedstock is fruit shells. Between the outer hull and the nutritious kernel lies the shell, primarily composed of cellulose, hemicelluloses and lignin. The valorization of such by-product could be an important way to add value to a low value product. Despite the existence of a number of published papers that have been reported the production of activated carbons from such by-product using different methodologies, adsorption applications, gasification of almond shells etc. [23,24,26]. There are a few studies about bio-oil production from this lignocelluloses source. Moreover, there are quite few studies about thermal degradation of HDPE in a pyrolysis reactor. According to our previous work, pyrolysis of aS gives 21% of bio-oil which can be considered as a low amount with compared to other biomass sources such as olive residues and cotton seed cake [23–26]. This study aims to increase the oil yield of aS pyrolysis with addition of a widely used polymeric waste (HDPE), a difficult thermally degraded disposal with compared to PP, LDPE [2,27,28].

In this study, HDPE is selected as a widely used plastic sample for the co-pyrolysis with a well-known lignocellulosic biomass source (aS) to investigate the synergistic effect on bio-oil yield and composition and understand the chemical transformations which could have taken place during the co-pyrolysis. Moreover, the co-pyrolysis of biomass and HDPE bio-oil was characterized in detail to determine its possibility of being a potential energy source and chemical feedstock.

2. Experimental

The almond shell (aS) taken from the city Mugla-Datca located in Aegean region, western part of Turkey was used as a biomass

sample, while HDPE was considered as a representative synthetic polymer. HDPE samples used in the experiments were supplied from a petrochemical company (PETKİM Aliğa, Turkey). The particle size of polymer sample was $D_p = 10 \mu\text{m}$. Air-dried biomass samples were ground in a high speed rotary cutting mill and screened to give fractions of $D_p > 1.8 \text{ mm}$; $1.8 > D_p > 0.85 \text{ mm}$; $0.85 > D_p > 0.425 \text{ mm}$; $D_p < 0.425 \text{ mm}$, $0.425 < D_p < 0.224$, $0.224 < D_p$. Average particle size was found to be as 1.67 mm.

Thermo Gravimetric Analysis (TGA) was applied by using Linseis Thermowaage L 81 thermo gravimetric analyzer coupled with Differential Thermal Analyzer (DTA) to evaluate the thermal behavior of aS and HDPE. Experiments were applied to 25 mg sample, 100 mL min^{-1} nitrogen flow with 10 °C min^{-1} heating rate. The TG and DTG curves for aS and HDPE recorded from room temperature to 1100 °C are shown in Fig. 1.

The pyrolysis experiments were performed using a fixed bed reactor (Heinze Retort). All detailed information about the system could be found in our previous studies [29,30]. The experiments were conducted at the atmospheric pressure. HDPE, aS and their mixtures (1:1; 1:2; 2:1) were placed in the reactor. Prepared 10 g of samples were put into the reactor. The reactor was heated from room temperature to the final pyrolysis temperature of 500 °C with a heating rate of 5 °C min^{-1} . The sweeping gas nitrogen is passed through the reactor at the gas hourly space velocity (GHSV) of 0.015 h^{-1} . The flow of gas released was measured by a rotameter for the duration of experiments. Experimental apparatus was held at adjusted temperature for 30 min. The liquid products were collected in ice-cooled traps. At the end of the experiments, the liquid product consisting of aqueous and oil phases were separated and weighed. All bio-oil yields were given water free basis. Char yield was determined from the overall weight losses of the reactor. The liquid product was weighed and recovered in dichloromethane for the further analyses. Water was determined by a separating funnel. Gas yield was determined by overall material balance.

All the yields were calculated on a dry-ash-free (daf) basis and each experiment was performed. The reproducibility of the experiments is acceptable and experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out three times within the experimental error of less than ± 0.5 .

The main analyses methods used to reveal the composition of bio-oil are elemental analysis, column chromatography, proton nuclear magnetic resonance spectroscopy ($^1\text{H NMR}$), Fourier transform infrared (FT-IR), column chromatography, and gas chromatography/mass spectrometry (GC/MS). This procedure that we used is illustrated in Fig. 2 and detailed about the analyses were given in our previous studies [29].

3. Results and discussion

3.1. Thermal gravimetric analysis of raw materials

The normalized weight loss (TG curve) and rate of weight loss (differential thermogravimetric curve (DTG)) for the aS and HDPE are shown in Fig. 1. The results show that the major weight losses of the aS and HDPE occur at 288.9 °C –345.4.6 °C and 470 °C, respectively. It can be seen that biomass sample decomposed at lower temperature than polymers while polymers begin to decompose 430 °C and showed the maximum mass loss around 470 °C (this can be seen from DTG of polymer) and about 500 °C, HDPE degraded completely without leaving any residue. As a consequence of TG/DTG curves of both materials, the optimum co-pyrolysis temperature was selected as 500 °C.

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