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Co-Pyrolysis of Olive Pomace with Plastic Wastes and Characterization of Pyrolysis Products

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Abstract**—**Waste polyethylene (PE) is classified as waste low density polyethylene (LDPE) and waste high density polyethylene (HDPE) according to their densities. Pyrolysis of plastic waste may have an important role in dealing with the enormous amounts of plastic waste produced all over the world, by decreasing their negative impact on the environment. This waste may be converted into economically valuable hydrocarbons, which can be used both as fuels and as feed stock in the petrochemical industry. End product yields and properties depend on the plastic waste composition. Pyrolytic biochar is one of the most important products of waste plastics pyrolysis. In this study, HDPE and LDPE plastic wastes were co-pyrolyzed together with waste olive pomace. Pyrolysis runs were performed at temperature 700°C with heating rates of 5°C/min. Higher pyrolysis oil and gas yields were observed by the using waste olive pomace. The biochar yields of HDPE- olive pomace and LDPE-olive pomace were 6.37% and 7.26% respectively for 50% olive pomace doses. The calorific value of HDPE-olive pomace and LDPE-olive pomace of pyrolysis oil were 8350 and 8495 kCal.

Keywords**—**Biochar, co-pyrolysis, waste plastic, waste olive pomace.

I. Introduction

SUSTAINABLE primary and secondary energy generation from biomass is of utmost importance considering the diminishing availability of fossil fuels and the higher sensibility towards environment preservation from pollutants generated by conventional energy production. Renewable energy derived from biomass reduces reliance on fossil fuels and it does not add new carbon dioxide to the atmosphere. Biomass is a term for all organic material that stems from plants including algae, trees and crops that are susceptible to be converted into energy [1].

Pyrolysis processing involves heating the material to moderate temperatures (400–700 _C) in the absence of oxygen. The organic components of the material are then decomposed, generating liquid (oil) and gaseous products, which can be useful as fuels and/ or sources of chemicals. The inorganic ingredients (e.g., glass and metals) remain practically unaltered and free of binding organic matter and therefore can be reused for certain applications (additive or fillers for other plastics) or, as a last resort, it would result in a much lower volume of waste to be placed in a landfill. Pyrolysis is especially appropriate for products or waste streams that contain waste plastics, organic waste and inorganic solid waste materials, as exemplified by the waste stream analyzed in this study.

Several studies have reported on the suitability of pyrolysis as a thermochemical recycling technique for plastics. However, mostof them have been conducted using individual plastics or plastic mixtures, which likely respond differently than real waste plastics to pyrolysis.

Biomass thermolysis has the potential to reduce our dependence on fossil resources by providing alternative fuels and specialty chemicals. Biomass pyrolysis is an important step in all thermolysis processes such as gasification, liquefaction and combustion [2]. Therefore, knowledge on pyrolysis products and related kinetics is essential in various energy and chemical production technologies [3]. Pyrolysis is an extremely complex process which goes through a series of reactions and can be influenced primarily by the temperature profile and pressure of the process [4]-[7]. The differences observed in the pyrolysis behavior of the ligno-cellulosic samples can be attributed primarily to the variations of hemicellulose, lignin and cellulose content of the biomasses [8].

Recently, biochar obtained from waste organic materials has shown the potential for improving soil fertility, carbon sequestration and water quality [9]-[12]. Biochar refers to the carbonaceous product from pyrolyzing biomass intended for soil application. The current market price of biochar is $2.20/kg [13].

During depolimerization, polymer chains are broken and new molecules of various sizes are created. Because most of these created molecules have radical character, they turn into gas, liquid and solid products by getting involved in a series of reactions among themselves [14], [15].

Plastics produced by petroleum products are composed of hydrocarbons. At the same time, they include a set of additive agents that are not environmentally desirable including antioxidants, colorants and stabilizers [16]-[18]. Plastic materials have proved their reputation and have gained popularity as they are light in unit weight, does not rust or rot, low in cost and, reusable. There are numerous of ways that plastic is being used nowadays/will be used in the near future. Hence, plastics have become essential materials and their applications in the industrial field are increasing. At the same time, waste plastics have created a very serious environmental challenge because of their huge quantities and their disposal problems. Plastics are produced from petroleum derivatives and are composed primarily of hydrocarbons but also contain additives such as antioxidants, colorants, and other stabilizers. PE is the third largest commodity plastic material in the world,

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after polyvinyl chloride (PVC) and polypropylene (PP) in terms of volume. PE is classified as LDPE and HDPE according to their densities. They are produced with low or high density addition polymerization of the molecule ethylene and with organometallic catalyzers. LDPE is phanerocrystalline, look like waxy and the polymer molecules are little branched, strong and its melting temperature is 110-125°C. HDPE is denser, less transparent and stronger polymers whose molecules are not branched. Its softening temperature is 137°C and durable to acids and alkalis. HDPE has a large area of usage. 40% of produced HDPEs are used in production of such plastic parts as bottles of drink, food, cleaning products, kitchenware, housewares and toys. 30% of it are used in packaging, thin film coating, productions of pipe, tube and cable [19].

Currently, disposing and recycling of plastic waste can be divided into four possible groups: landfills, incineration, mechanical recycling and chemical recycling. Landfills cause more and more serious problems because of the environment load, due to the filling of the landfills and the cost consumption is increasing, therefore significant efforts are being made to increase recycling and re-processing in Europe. Energy produced from plastic waste by burning is very disputable. However plastic waste has a high heating value (the heating value of the polyolefins (43.3 MJ/kg) is almost the same as that of the fuel oil (44 MJ/kg), and it is higher than the heating value of good quality coal (29 MJ/kg)), and the waste incineration can pollute the air and environment. E.g. if the incinerators do not operate properly, the dioxin, furan derivatives and the heavy metals in the smoke can cause great environmental problems. The mechanical recycling is a process in which the clean and homogenous plastic are granulated and new products are made by e.g. injection molding. The mechanical recycling is economical only in cases when high purity selectively collected wastes are available, but also in that cases the profitability of the method should be very low. According to papers the most prospective route for plasticwastes utilization is the so calledchemical recycling, when the long carbon chains of polymers are cracked thermally and result in the mixtures of gases and liquid hydrocarbons. Products can be used for different purposes, for example polymer can be made from the decomposed product, or they can be used in other chemical processes such as in oil refining, where they can be made into raw chemical materials together with the mineral oil fractions. The preferred plastics for chemical recycling are polyethylene, polypropylenes and polystyrene, that is to say their products show similar properties like petrochemical feedstocks. The pre-treatment and source of plastic wastes can considerably modify the end product properties. Sometimes impurities have attached on the surface of plastic wastes, which deteriorate the favourable properties of gasoline, oils, etc. Therefore researchers quite often have focused on the pyrolysis of granulated, pure plastics, which are not real wastes [20–26].

The use of plastic materials in a variety fields has led to the generation of an increased amount of plastic wastes and due to the increased environmental awareness and depletion of natural oil deposits, the converting of waste plastics into liquid hydrocarbons is being considered a promising recycling method. For liquefaction of waste plastics, pyrolysis may provide a suitable means of recycling, of great interest both economically and environmentally.

Waste plastic mainly consists of polyethylene (PE), polypropylene (PP) and polystyrene (PS) with different polymer structure, which is above 70% in waste plastics. Thus, recycling of waste plastic is highly encouraged. With respect to the method of recycling, plastics can be practically recycled either mechanically towards a new plastic with a lower grade application, i.e., physical recycling, or chemically to obtain chemical raw materials or fuel oil, i.e., chemical recycling. However, physical recycling, as a conventional method to treat the waste plastic mixture, is limited by technical problems, difficulties in maintaining the product quality and adequate price .Thus, physically recycled plastics should be treated by other procedures such as chemical recycling and energy recovery.

Nowadays, wastes such as plastics, used tires and lignocellulosic biomass are, presently, generated in huge amount and considered as suitable raw materials for pyrolytic processes. By this process, natural and synthetic polymers are broken down into smaller hydrocarbon chains. The products formed include solid product (char), gas and pyrolysis oil that have industrial and energetic applications.

In this study, HDPE and LDPE plastic wastes were co-pyrolyzed together with waste olive pomace. The effect of the waste olive pomace/waste plastic ratio to the product properties was investigated.

II. Materials and Methods

Waste HDPE and LDPE was crushed into approximately 8 mm pieces in plastic crusher. These waste plastics were pyrolysed at fixed bed reactor pyrolysis equipment. The crushed materials were pyrolysed at 700°C under a heating rate of 5°C/min in a chromium reactor (Fig. 1).



Fig. 1 Pyrolysis System

At the end of pyrolysis processes, char, oil and gaseous products were collected. The gas product was collected in gasometer system.

TGA tests were carried out under an inert atmosphere (N_2) using a TGA-Q-500, TA Instruments equipment. Heating rates

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were controlled at 20 °C/min. Experiments were performed under a nitrogen atmosphere with a flowrate of 100 cm^3/min. The thermal behavior of the char was studied through TGA in the temperature range of 0-900°C.

The heating value of the oil samples were measured by using a cylinder (bomb) type auto calorimeter (AC-350, LECO).

III. Results and Discussion

A. Pyrolysis Yields

The yields of pyrolysis products were given in Table I.

TABLE I
PYROLYSIS YIELDS OF HDPE, LDPE AND OP

	%wt		
	Char/Biochar	**Oil**	**Gas**
HDPE	2.14	83.36	14.0
LDPE	6.44	72.85	20.71
OP	10.05	71.54	18.41
50%HDPE +50%OP	6.37	68.22	25.41
50%LDPE+50%OP	7.26	59.15	33.59

Gas productions of the LDPE plastic wastes were higher as compared to HDPE pyrolysis. Condensation temperature of the LDPE produced under high pressure was lower than the HDPE produced under low pressure [14]. Therefore, gas produced through the pyrolysis of HDPE plastic wastes was easily condensed as compared to LDPE the plastic wastes at the same temperature conditions and less gas product yield was obtained. The amount of liquid product captured in liquid condensation cabs of the system is 83.36% and 72.85% for HDPE and LDPE, respectively, at 700ºC. 2.14% of HDPE char remained at pyrolysis temperature of 700ºC. As temperature increased, char turned into new gas products. It must be noted that HDPE and LDPE are polymers in the group of polyolefin, the yield of liquid product is generally higher than the yields of solid and gas product in pyrolysis of these types [27]. Depolymerization increased and molecular weight of polyethylene and the number of double bond in polymer decreased in the plastic wastes for HDPE as temperature increased LDPE, depolymerization more slowly occurred as compared to HDPE because this type of plastic is produced under high pressure conditions.

10.05% of olive pomace (OP) char remained at pyrolysis temperature of 700ºC. During the primary pyrolysis of OP, thermal cracking of chemical bonds in the individual constituents of the pomace, which are mainly cellulose, hemicelluloses and part of the lignin, takes place and permanent gas species (e.g. CO_2, CO, CH_4) and condensable species at ambient conditions (several organic compounds and water) are evolved. During the secondary pyrolysis, serial and parallel reactions take place, occurring either heterogeneously or homogeneously, as for example cracking, reforming, dehydration, condensation, polymerization, oxidation and gasification reactions [28]-[36].

Pyrolysis of OP alone produced 10.05% solid products (i.e., biochar), while co-pyrolysis of 50%HDPE+50%OP and 50%LDPE+50%OP produced 6.37% and 7.26% biochar, respectively (Table I). This reduction in biochar yield of the mixed feedstock was due to the presence of plastics which have lower char yields. The gas production was 25.41% for 50%HDPE+50%OP, and 33.59% for 50%LDPE+50%OP. Gas produced through the pyrolysis of OP with HDPE was easily condensed as compared to the plastic wastes of OP with LDPE at 700°C and less gas product yield was obtained.

B. Pyrolysis Liquid Product Heat Values

In Fig. 2 the effect of plastic type and of co-pyrolysis on heating value of liquid products is presented.

The heating values of HDPE and LDPE oils were 4923 kCal and 4596 kCal, respectively. The most common oil components of these plastics found were ethane, propane and n-butane which are inert combustible hydrocarbons [24], [25]. Therefore, heating values were similar. Consequently, 50%HDPE +50%OP and 50%LDPE +50%OP groups showed similar heat values as 8350 kCal and 8495 kCal which are closer values to the heating value of OP, 745 kCal. Heat values of HDPE and LDPE pyrolysis oils were much lower; therefore, it can be inferred that OP biomass helps the improvement of heat values of these oils. The composition of the pyrolysis oil of OP is given in literature OP contains primarily alkenes, esters, aromatics, ketones and alcohols with different oxygen containing functional groups [29]. Consequently, the highest heating value was obtained for OP.

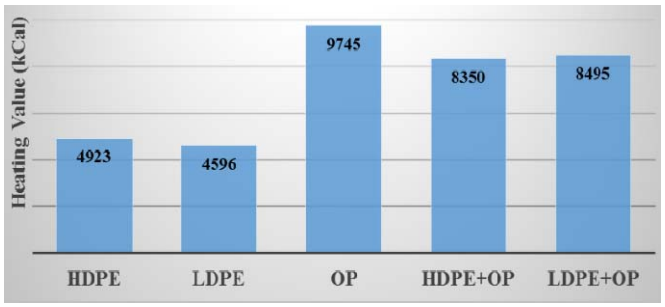


Fig. 2 The heating values of pyrolysis oils

IV. Conclusions

The co-pyrolysis of waste HDPE and LDPE with OP was investigated. Pyrolysis yields of HDPE and LDPE plastic wastes were 97.86% and 93.56% respectively. The characterizations of the oil products have shown that the 50%HDPE +50%OP (8350 kCal) and 50%LDPE +50%OP (8495 kCal) obtained can be used as fuel or can be utilized in the process itself to reduce the input energy sources and helps to become self-sustainable process. Co-pyrolysis also improved the pyrolysis gas production efficiencies by the help of biomaterial in the system. Produced pyrolysis gas has also potential to be used as fuel.

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