



Efficient disposal of waste polyolefins through microwave assisted pyrolysis



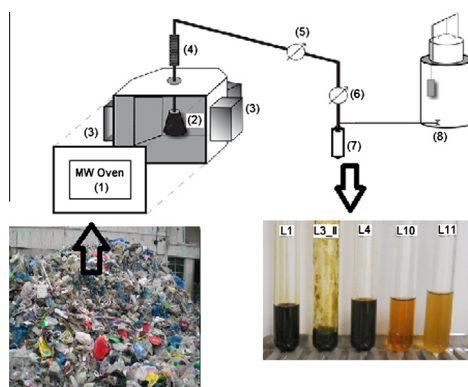
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HIGHLIGHTS

- Microwave assisted pyrolysis of HDPE and PP was run.
- HDPE and PP were converted into low viscosity liquid.
- Aromatics were not formed from MAP of HDPE.
- Aromatic were formed from pyrolysis of PP.
- Different microwave absorber were tested in HDPE and PP pyrolysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Waste or contaminated polyolefins were disposed through microwave assisted pyrolysis (MAP) using tires or carbonaceous char as microwave (MW) absorber. High density polyethylene (HDPE) was converted into waxy products when standard heating was employed. However HDPE was converted into a low viscosity fraction by using a very low MW power, but a not completed conversion was achieved while PP was always converted into a liquid having a low viscosity. Using an oven containing a system able to fractionate the vapor formed, the residence time of the waxy products in the oven was improved together with the overall pyrolysis efficiency. However the time of the process was strongly reduced with respect to processes using a classical heating. The liquid fraction from HDPE contained linear alkanes and 1-alkenes with negligible formation of branched, cyclic, or aromatic hydrocarbons, while liquid from PP was formed by a mixture of methyl-branched alkane and alkenes, and sometimes aromatics as a function of pyrolysis conditions.

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1. Introduction

Nowadays polyolefins are the most and widely exploited polymeric materials for any technical or packaging use. In 2011 even if the European polymer industry was affected by the financial crisis a turnover increase of 0.3% was achieved. Among polyolefins, polyethylene (PE) and polypropylene (PP) are the most widely used

with a production of 13.6×10^9 kg and 8.9×10^9 kg respectively that is 29% and 19% of the overall demand of plastics in 2011. As a consequence large amount of polymeric waste were produced, approximately 26×10^9 kg, and a large amount of them (10×10^9 kg) were not recyclable and sent to landfill. Their widespread use arise the economic and environmental problem of their resourceful disposal [1].

Valorization of waste polyolefins may follow three paths: (1) material recovery through direct reprocessing by extrusion or molding; (2) thermal treatments devoted to energy recovery; (3)

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landfilling if any of the previous ways are not possible [2,3]. Material recovery is the preferred strategy but it can be performed only on homogenous and not polluted waste stream. In fact different classes of melted polyethylene are not miscible. Furthermore recycle can be performed for a limited number of times, due to a gradual loss of the technological performances. Among thermal treatments, incineration may allow energy recovery but the chemical content is completely lost and it may lead to the emission of pollutants. Landfilling is an even worse perspective for waste polyolefins due to the total loss of material and energy, furthermore their low density and long degradation time cause a rapid and long term filling of landfill sites [4].

In the last two decades a remarkable attention has been paid to pyrolysis as promising technology for polymeric waste disposal. Pyrolysis is a high temperature treatment (over 700 K) breaking polymeric macromolecules to compounds having a lower molecular weight. It is usually performed in an inert, not oxidizing, environment and three classes of products are obtained: a gas (volatile hydrocarbons), a liquid/wax (condensable hydrocarbons), and a char (coking products and inorganic compounds such as fillers stable to pyrolysis conditions). Problems connected with polyolefins pyrolysis arise from their poor heat conductivity and several methodologies and technologies were developed to overwhelm this problem.

Furthermore cleavage of C–C bonds requires a higher activation energy for PE than PP, respectively 225 kJ mol^{-1} and 176 kJ mol^{-1} [5]. The lower energy requirement, for PP, was linked to the presence of tertiary carbon atoms in the main chain which let a more efficient cracking and the formation of tertiary radical intermediates more stable than secondary one formed by PE.

A pyrolysis system with a good heat transfer promoted a fast and efficient degradation. In a fluidized bed reactor (characterized by a very efficient heat transfer) PE, and PP are pyrolyzed giving waxes, a low viscosity oil [6], and even aromatic hydrocarbons (BTX) [7], while in conical spouted bed reactor (heat transfer is less efficient) a wax is the sole product [5].

High grade products, especially connected with the liquid fraction, may be obtained using a catalytic system such as: zeolites [8–11], basic salts [12], and Zigler–Natta catalyst [13,14] but the catalyst must be frequently regenerated.

Polyolefin pyrolysis is driven by a series of homolytic bonds cleavage through a radical mechanism and the main products in PE pyrolysis are linear alkanes, their corresponding 1-alkenes (from C1 to C54), naphthenes, and aromatic compounds [6]. Usually in classical pyrolysis, when the heat transfer is not optimal, the main product is a wax or a high viscosity liquid, semi-solid at room temperature. Meanwhile PP pyrolysis gives branched alkanes, and alkenes together with aromatic compounds [15]. Furthermore PP may be used as starting material for production of carbon nanotubes, using a catalyst and specific pyrolysis conditions [16,17].

In the last few years microwave (MW) heating has encountered a sound and reliable application in polymeric waste treatments [18–21]. Among them microwave assisted pyrolysis (MAP) encloses a number of advantages over classical methods. One of these achievements is the direct and extremely fast heating of any material able to turn MW into heat. Polymers are usually transparent to MW and an absorber is required for MAP of plastics [22–24]. Metals (as wire or powder), or carbon (in almost any form) are very efficient materials to convert MW radiation into heat (at a frequency of 2.45 or 0.972 GHz, the only two available for commercial heating supplies), and they are suited for any MAP applications [25]. MAP of PE was previously investigated [23] and several efforts were devoted to improve the quality of products, especially for the liquid fraction [24]. Information over MAP of PP can be extrapolated only from patent literature [26] and any industrial, large scale, application is not foreseen to be available to the best

of our knowledge. So far implementations of MAP of PE and PP are mandatory to allow any commercial use of this methodology.

Ludlow–Palafox and Chase reported MAP of PE in the presence of carbon black as MW absorber, and a waxy liquid was obtained as the main product together with low amount of gas and char [23]. Switching to a specific active carbon as the MW absorber, which interacts in a different and more efficient way with MW, the liquid is a diesel oil while the waxy fraction is not formed [24].

In this paper we have studied MAP of waste high density polyethylene (HDPE) and PP in different experimental conditions aiming to obtain a liquid mixture of linear hydrocarbons, fluid at room temperature. Low density polyethylene (LDPE) was not tested because, due to its structure containing several chain branching, it could have an intermediate behavior between HDPE and PP. Chopped tires or a carbon, obtained from previous experiments by Undri et al. of MAP of tires [27,28], were employed as MW absorber.

2. Experimental section

2.1. Materials

A polyethylene flask, a polypropylene container, and a commercial tire (Michelin model Agilis 81-195/65 R16C) were chopped to a $2 \times 2 \text{ cm}$ chips, and dried for 24 h at 338 K in a ventilated oven before each experiment. Representative samples were characterized via ultimate analysis (HDPE: C: 85.10%, H: 14.90%, ash: 0.02%. PP: C: 81.35%, H: 13.60%, ash: 5.50%. Tire: C: 88.19%, H: 7.23%, N: 0.23%, S: 1.76%, ash: 2.18%). The carbon powder, employed as MW absorber was obtained from MAP of tires and characterized via ultimate analysis (C: 87.99%, H: 0.58%, S: 1.80%, ash: 7.53%).

2.2. Instruments

Pyrolysis were carried out in a MW oven working at 2.45 GHz, designed and supplied by Bi.Elle s.r.l. – Italy. Two experimental set-ups were used and their description was previously reported [27–29]. The first one was equipped with an oven with four external MW generators each having an absorption of 2 kW electric power for a total of 8 kW, capable of delivering up to 6 kW of microwave power inside the oven [27]. The oven was equipped with a wide angle measuring infrared thermometer, which provides information on the overall temperature inside the oven but not the temperature on the sample surface. This equipment was called set-up A. The other equipment, called set-up B, used the same MW oven but a fractionating column was placed between the oven and the condensing system. The column had a length of 0.2 m, internal diameter of 0.03 m, it was filled with glass spheres having a diameter of 4.0 mm. This fractionating system avoid to high boiling fractions to leave the oven [26].

Kinematic viscosity was detected with an Ostwald viscometer at 298.14 K; using a Julabo model ME-18V thermostat. Cyclohexane, chlorobenzene and 1,4-dimethylbenzene were used as standards [30].

Density was determined with a pycnometer thermostated at 298.14 K.

CHN analysis was performed using a Perkin–Elmer CHNS/O Analyzer model 2400 Series II.

Calorific power (higher heating value, HHV), together with sulfur content of the products were detected by an external laboratory, ESSE.T.I.A. s.r.l. – Italy using a homemade bomb calorimeter.

The ash content was evaluated according to ASTM D 2866-94 method.

Infrared (FTIR) analyses were performed with a Shimadzu model IRAffinity-1, equipped with a Golden Gate single reflection diamond ATR accessory supplied by Specac.

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