



Microwave pyrolysis of polymeric materials: Waste tires treatment and characterization of the value-added products

Andrea Undri, Stefano Meini, Luca Rosi, Marco Frediani, Piero Frediani*

Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 3-13 Sesto Fiorentino, 50019 Firenze, Italy

ARTICLE INFO

Article history:

Received 18 June 2012

Accepted 17 November 2012

Available online 6 December 2012

Keywords:

Microwave pyrolysis

Waste tire

Carbon

Oil

Liquefied petroleum gas

ABSTRACT

Waste tires are well known to have relevant disposal or reprocessing problems under environmental and economic sustainable conditions. These processes may be a challenge for industrial and academic research. In this contest pyrolysis represent a modern valid alternative to undergo treatment of waste tires as long as it will be possible to generate value-added products. Anyway improvements in the heat transfer technology are crucial to optimize the efficiency of the process itself. Here we describe the use of microwave (MW) irradiation as one of the most promising heating technologies for pyrolysis, due to its ability to heat quickly and directly any MW absorbing material. Experiments were run in a batch laboratory scale with an oven operating at a frequency of 2.45 GHz with a variable energy output up to 6 kW. A special attention was dedicated to the influence of operating variables on liquid product properties. The reaction was performed in a short time comparing with traditional heating techniques and the most performing conditions were achieved using a MW power of 3 kW per 0.2 kg of tires. Typical products were a solid residue (char) containing up to 92.03% of carbon and appreciable quantities of mineral matter, a low viscosity oil (<2.9 cP, with a large amount of single ring aromatic hydrocarbons) and a gas containing light hydrocarbons, hydrogen and only traces of N₂. The three products collected had a high calorific value, respectively 34 MJ/kg for solid, 45 MJ/kg for liquid, and 46 MJ/kg for the gas fraction.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The worldwide consumption of polymeric materials is growing ceaselessly even in spite of the financial crisis. World's plastics production in 2009 was 2.3×10^8 tons and 4.5×10^7 tons in Europe. A large part of this production (54%) is disposed as waste [1,2].

Thermoplastic polymers are directly recyclable as starting material if they are collected as a homogeneous stream of waste. For instance, polyethylene or polyethylene terephthalate, used in packaging industry, are efficiently recovered, reprocessed and sold as pipes and fibers [3].

A mixed stream of several plastic or composite waste are directly recycled in a more subtle way. Among polymeric composites, tires are extremely complex items, which contain synthetic and natural rubber, metal wire, carbon, sulfur compounds and other additives used in the vulcanization and molding processes [4]. Their production is going over 2.8×10^8 units/year and waste tires are well known to present formidable disposal or reprocessing problems. To the best of our knowledge end use tires meet four different paths:

material recovery, energy recovery, landfill or unknown destination [5].

Material recovery could be the most appealing way to deal with tires. The reconstruction of tires shows the highest material and energy recovery. However this procedure is limited by the quality and deterioration of end use tires and it can be repeated no more than two times [5]. Tires which are not suitable for reuse or remanufacture can be used in engineering works for many applications, such as roads (asphalt, where the granules improves the mechanical strength, reduces noise and eliminates the aquaplaning), street furniture (beds for curbs, bollards, bike paths, parking lots, play areas), sports (football pitches in synthetic grass and sports flooring for athletic tracks) and as a filling material for new tires production (in ground form) [5].

Energy recovery could be a good way to manage waste tires disposal. They have a higher calorific power and a lower CO₂ emission, than commercial carbons [6]. Tires are then used as energy source, whole or more often chopped in cement and paper factories where the overall energy consumption is high and a slow combustion is required. They can reduce the emission of common pollutants in cement factories (NO_x, SO₂ and dioxins) if they substitute the petroleum coke [7]. Finally their application in thermoelectric power plants follows the same reasons: high energy content and low emission of pollutants.

* Corresponding author. Tel.: +39 055 4573522; fax: +39 055 4573531.

E-mail address: piero.frediani@unifi.it (P. Frediani).

Landfill or even worse unknown destination should be avoided. In Europe the whole tires, and chopped tires, cannot be sent to landfill anymore (Council Directive 1999/31/CE). The aim behind these laws can be clarified if the properties of waste tires are considered: high heating value but low thermal conductivity (long burning time); low apparent density (125 kg m^{-3}), given by the tire typical round hollow shape (inclusion of air inlet which can keep a fire alive); emission of polluting gases and particles during an uncontrolled combustion [8]. The unknown destinations are without any uncertainty the most environmental dangerous disposals, tires can be sold without any control to developing countries with less strict laws or can be piled up in illegal landfill [2].

The above reported technologies are not enough proper to deal with the whole amount of end used tire, for instance 13% of scrap tires produced in U.S.A. were sent to landfill or unknown destination in 2010 [2]. Therefore the disposal of waste tires is a serious environmental problem against which public is becoming more aware. For these reasons research on reuse and recycling of tires are an actual and challenging subjects.

A pyrolysis process works in absence or in the presence of low amount of an oxidant, it can be an interesting alternative to other processes, because it allows to transform tires in three useful classes of products: a solid, a liquid and a gas [9]. These products can be easily stored, transported and used as a source of energy and chemicals. Pyrolysis can be performed with several heating technologies, which are characterized by different equipment and experimental parameters. The most important and typical parts of these plants are the furnaces and the heat transfer technology because tires usually show a very low thermal conductivity. The scientific literature reports a wide selection of pyrolysis layout: autoclave [10,11], static-bed reactor [12–14], moving bed reactor [15,16] and rotary kiln [17]. A comparative study is not easy to do because many parameters vary among each pyrolysis arrangements. The differences can be summarized in substrate (tire) size, reactor form, pyrolysis temperature, residence time inside the reactor and heat transfer system. In many pyrolysis experiments the heat is provided by a source external to the reactor, usually an electrical resistance but it may be also supplied by partial combustion of tire itself [9].

Microwave (MW) [18] is one of the most promising heating technologies for pyrolysis due to its ability of heating quickly and directly any MW absorbing material [19–24]. Polymers do not have the ability to absorb MW and turn them into heat. Anyway it is possible to pyrolyze them if they are mixed with a MW absorbing material [25,26]. Tires contain carbon black, up to 30% (wt%) and metal wires which are excellent MW absorbing materials. Carbon black is able to turn the MW radiation into heat in few seconds: a temperature of 1556 K is reached in 120 s using a power of 600 W [27]. Patent literature provides a large amount of information over the state of art of MW pyrolysis of tires [28,29]. The data are mainly referred to the apparatus and experimental set up but few data are reported on the yields and properties of the products which are usually characterized as fuel. The plant shows the common parts identifiable in any non-MW pyrolysis equipment: reactor, cooling system of the products and collecting devices for liquid and gas.

We report our results over the MW pyrolysis of chopped tires performed in a batch reactor operating at a MW frequency of 2.45 GHz with a variable energy output up to 6 kW. We highlight the good performance of a simple set-up, avoiding the use of a carrier gas and transforming tires into useful chemicals.

Different experimental parameters were tested to afford the best conditions even if they were not fully optimized. The influence of parameters such as MW power and tire mass was investigated with a special attention to their influence on the yield and product features. Finally because temperature measurement is a

challenging aspect under microwaves conditions, experiments were run using infrared and fiber optic thermometers.

2. Experimental

2.1. Materials

A commercial tire (*Michelin* model *Agilis 81–195/65 R16C*) was chopped to a $2 \text{ cm} \times 2 \text{ cm}$ chip. The tire chips were dried for 24 h at 338 K in a ventilated oven before each experiment. A representative tire sample, metal wires depleted, was characterized via ultimate analysis (C: 88.19%, H: 7.23%, N: 0.23%, S: 1.76%).

2.2. Instruments

The pyrolysis were carried out in an oven (Fig. 1) with four external MW generators (2) 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. It was designed and supplied by Bi.Elle s.r.l. (Via Ho Chi Min, 6, Modena, Italy). The oven was also 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.

A fiber optic thermometer Ultra OptoTemp 2000 was sometimes used, with a temperature range from 473 K to 1223 K, placed on the top of the vertical glass pipe and kept in direct contact with the tire chips during the whole experiment. This contact thermometer was crucial to understand and record the correct pyrolysis temperature which is discussed in Section 2.4.

An Ostwald viscosimeter thermostated with a *Julabo* model ME-18 V at 298.14 K, filled with silicone oil, was used to evaluate the kinematic viscosity of liquids. Cyclohexane, chlorobenzene and 1,4-dimethylbenzene were used as referring standards [30].

The density of liquid was checked with a pycnometer thermostated at 298.14 K. The apparent density of the solid products was evaluated according to ASTM method D 2854-00.

The CHN analysis was performed using a Perkin-Elmer CHNS/O Analyzer model 2400 Series II. The calorific power (higher heating value or gross calorific value (HHV) and lower heating value or lower calorific value (LHV)) together with the sulfur content of the products were detected by an external laboratory, ESSE.TI.A. srl (Via dell'arte della paglia 3, Campi Bisenzio, Italy) using a homemade bomb calorimeter.

The infrared (FTIR) analyses were performed with a Shimadzu model IRAffinity-1, equipped with a golden gate single reflection diamond ATR accessory supplied by Specac.

The gas chromatographic analyses of liquids were performed using a Shimadzu GC-MS QP5050A equipped with a capillary column Petrocol™ DH 24160-U (100 m length, 0.25 mm diameter, 0.5 μm stationary phase), using a 1:30 split ratio and a quadrupole mass (MS) detector with electron ionization, operating in the mass range 40–450 m/z . The oven operated at 298 K for 15 min, then heated at 2.5 K/min up to 523 K and kept at this temperature for 15 min. Other significative peaks were not detected at higher temperature. The total ion chromatography (TIC) was obtained with a signal-noise ratio of five, and the area percentage was reported without any response factors correction. The compounds were identified using the NIST mass spectra library.

The gas chromatographic analyses of gases were performed using two different instruments equipped with a flame ionization detector (FID) or a thermal conductivity detector (TCD). The GC-FID analysis was carried out with a Shimadzu GC-2010 working with a capillary column Supelco SPB-5, 60 m length, 0.25 μm stationary phase, 0.25 mm diameter, column flow 0.98 mL/min. The sample was injected using a 1:30 split ratio. The gas chromatograph

Download English Version:

<https://daneshyari.com/en/article/1197182>

Download Persian Version:

<https://daneshyari.com/article/1197182>

[Daneshyari.com](https://daneshyari.com)