



# Reverse polymerization of waste polystyrene through microwave assisted pyrolysis



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## ABSTRACT

Reverse polymerization of waste polystyrene (PS) was exploited to produce styrene and other aromatics through microwave assisted pyrolysis (MAP), due to the benefits associated with microwave (MW) heating. MAP of PS was run by varying MW power and absorber (tire and carbonaceous char from MAP of tire). A clear and low viscosity liquid containing styrene was always collected as the major product, together with low amount of char and gas. Using a MW power of 3 kW and 100 g of PS together with 47.3 g of carbon gave a liquid (yield 86.5%) containing higher amount of single ring aromatic compounds, as evaluated by GC–MS (aromatics C6–C10 93.9%, styrene 66.0%) a char (yield 9.8%) and a gas (yield 3.7%). Improvements in residence time, by using low MW power or a fractionating system directly inserted over the oven and before the collecting system, allowed us to obtain a liquid with low viscosity and density even if the char yield was 10.0%. Liquid was characterized through physical (density, viscosity, high heating value), and chemical tests (elemental analysis, GC–MS and FT-IR).

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## 1. Introduction

Polystyrene (PS) is the most employed aromatic thermoplastic polymer. PS finds a wide range of application from food contact packaging to thermal insulator in buildings. In 2011 the European production of PS was  $3.5 \times 10^9$  kg, and its disposal is an environmental and social problem which is ceaselessly addressed from academic and industrial researchers [1].

Among several recycling processes exploited, the most used is direct remanufacturing through milling, washing, drying, and moulding but this is possible only for uncontaminated waste [1,2].

Otherwise aromatic feedstock are usually obtained from catalytic refining of oil fractions, indeed the safeguarding of energy and material content of waste PS is a key point for saving oil stocks [3]. PS and specially contaminated PS may be disposed through chemical recycling and among these methods the preferred one focus on the conservation and valorization of the phenyl moiety widely present in PS. Pyrolysis meets these requirements: it may convert waste PS into single ring aromatic compounds, together with low amount of char and gas, if appropriate pyrolysis conditions are employed [4–7].

PS pyrolysis is driven by free radical reactions that may act with three different competitive paths accordingly to radical formed: chain-end, near chain-end, or random internal position. The fate

of these radicals is:  $\beta$ -scission to give an alkene and a smaller radical, or hydrogen transfer from another molecule to form a saturated hydrocarbon and a new radical, or intra-molecular hydrogen radical transfer with formation of an alkane and an alkene [8,9]. Pyrolysis of PS is already active at 623 K, where the main product is a dark viscous liquid rich in single ring aromatic compounds (benzene, toluene, ethylbenzene, and styrene). Char formation increases when pyrolysis temperature raises [6]. The char may be formed by condensation between neighbouring phenyl moieties. Anyway different pyrolysis behaviour is observed for different classes of PS (virgin, expanded, and compacted from containers), especially for what concerning the composition and distribution of aromatics in the liquid fraction [10].

The use of a catalyst may improve the production of some specific aromatic compounds, such as styrene but the catalyst may be rapidly deactivated by char formation [11–16]. Improvements of styrene were also achieved using different fluidizing medium, such as quartz sand in a fluidized bed reactor [4], light-cycle-oil [17], or tar pitches [18]. Alternatively catalytic degradation of PS may lead to the formation of molecular hydrogen in a two steps process in the presence of a Ni catalyst [19].

In the last few years microwave (MW) heating has encountered a sound and reliable application in polymeric waste treatment [20–22]. Microwave assisted pyrolysis (MAP) encloses a number of advantages than classical methods. One of these is the direct and extremely fast heating. Polymers are usually transparent to MW [23] and need an absorber to run MAP [20,21,24–27]. Metals [28,29], or carbon [20,30] are very efficient to absorb MW and

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convert it into heat. These MW absorbers are suitable for any MAP applications and they reach a very high temperature in a short time. Sometimes localized spots of very high temperature were generated due to the formation of plasmas [31]. MAP of PS has been investigated in the presence of iron mesh [28], or aluminium as coil or mesh [32,33] as MW absorber. Iron can reach temperature up to 1470 K, and the main products collected were styrene, ethylbenzene, and condensed ring aromatics, but data about their relative abundance were not reported [28]. Using aluminium in various shapes and arrangements high temperatures were also achieved (aluminium melting point is 993 K); the best performance were achieved with a coil which allows to convert PS in 88 wt% of a liquid, but also these authors did not report any information concerning quantitative composition of products [33].

In this paper MAP of PS was investigated using different MW power, MW absorber (tire and carbonaceous char from MAP of tire) [21,26,34], and apparatus set-up with the aim to produce large amount of a low viscosity styrene enriched liquid, together with low amounts of char and gas.

## 2. Experimental

### 2.1. Materials

Scraps of expanded PS recovered from clean waste boxes used for freight of chemicals were heated at 380 K, over its glass transition temperature, to form flakes of  $2 \times 2$  cm to facilitate the reactor filling. A commercial tire (Michelin model Agilis 81 – 195/65 R16 C) was chopped to a  $2 \times 2$  cm chips (a more detailed description was reported by Undri et al. [21,26]). The carbon powder, employed as MW absorber was the solid from MAP of tires [26] (No pre-treatments on carbon powder were run). Samples were dried for 24 h at 338 K in a ventilated oven before each experiment. Representative samples were characterized via ultimate analysis (PS: C: 92.10%, H: 7.84%, ash: 0.76%. Tire: C: 88.19%, H: 7.23%, N: 0.23%, S: 1.76%. Carbon: C: 87.99%, H: 0.58%, S: 1.80%).

### 2.2. Pyrolysis unit and details

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 [22,26]. The first one was equipped with an oven with four external MW generators, each having an absorption of 2 KW electric power, able of delivering up to 6 KW of microwave power inside the oven [24]. 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 30.0 mm, it was filled with glass spheres having a diameter of 4.0 mm. Figures of the two set-ups are reported as supplementary materials (Figs. S1 and S2). This fractionating system avoid to high boiling fractions to leave the oven [25].

Samples were placed in a 1000 cm<sup>3</sup> borosilicate Erlenmeyer flask inside the oven and connected with two condensing systems cooled at 298 K and 263 K, respectively (experimental set-up A, experiment 1–5, 7, and 8 Table 2). Liquids were collected in a flask and gas in a gasometer. A fractionating system inserted over the oven and before the condensing system was used in experiment 6 (set-up B). An illustration of both experimental set-ups is provided in the supplementary materials and further details in ref. [21,22,24–26].

All experiments were carried out in an anoxic atmosphere without any carrier gas avoiding the dilution of gas products, preventing the formation of nitrogen containing compounds, and simplifying the equipment. The gas flow was achieved by the gas formed during pyrolysis, the pressure fall provided by the condensing system and the gasometer.

In a typical pyrolysis PS chips were mechanically mixed with the MW absorber prior the pyrolysis, then heated according to parameters reported in Table 1. Set-up, MW power, and MW absorber were the investigated parameters. Pyrolysis was stopped when gas evolution was not further detected.

Yields were calculated excluding metal wires present in tire (experiment 7 and 8).

### 2.3. Analysis of liquid

Liquids were centrifuged at 2000 rpm for 10 min and then filtered to evaluate if any particulate was present.

Kinematic viscosity (ASTM method D 2854-00) was detected with an Ostwald viscometer thermostated with a Julabo model ME-18 V at 298.14 K. Cyclohexane, chlorobenzene and 1,4-dimethylbenzene were used as standards [35].

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.

Heating values (higher heating value (HHV)) and sulphur content were detected by an external laboratory, ESSE.TI.A. srl, (Italy) using a homemade adiabatic bomb calorimeter. Lower heating value (LHV) was calculated taking into account HHV and ultimate analysis.

Ash content was evaluated according to ASTM method D 2866 – 94.

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

Gas chromatographic analyses 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 operating 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. A quadrupole mass (MS) detector, with a 70 eV electron impact ions generator, operating in the range 40–450 m/z was used. Other noteworthy peaks were not detected at higher temperature. Total ion chromatography (TIC) was obtained with a signal/noise ratio of five, and composition was reported as percent peak areas without any response factors correction. Compounds were identified using the NIST mass spectral library.

## 3. Results and discussion

### 3.1. Pyrolysis experiments: yields

Microwave assisted pyrolysis (MAP) of PS was investigated by varying three parameters: microwave power, microwave absorber, and apparatus set-up (Table 2). Although temperature plays an important role, this parameter is uncertainty detected in MAP, as previously reported by Undri et al. [26,34] and by Bykov et al. [36], and the maximum temperature reached was reported in Table 2 but it was not used as a descriptive parameter.

During MAP absorber was initially heated, the heat transferred to the polymer that was melted, then the absorber was incorporated into the melted PS and pyrolysis went.

PS in the presence of carbon as MW absorber was almost completely converted into a liquid fraction using MAP (experiment 1,

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