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Microwave Pyrolysis of Polymeric Materials

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1. Introduction

The consumption of polymeric materials is growing ceaselessly in the world even in spite of the financial crisis.

World's plastics production in 2009 was $2.3 \cdot 10^8$ tons and in Europe it was $4.5 \cdot 10^7$ tons whose 54% is disposed as waste. The annual average production of tires in Europe is more than $2.5 \cdot 10^6$ tons. In the 2008 in Italy were produced $3.5 \cdot 10^6$ tons of plastics among which $4.1 \cdot 10^5$ tons of tires, and $1.5 \cdot 10^6$ of waste plastics tons were collected for disposal. (Chen et al., 2007; Federazione Imprese e Servizi, Unione Nazionale Imprese Recupero [FISE UNIRE], 2009; PlasticsEurope, 2010).

World rubber demand is foreseen to increase up to 4% annually to 26.5 million metric tons in 2011 (Freedonia, 2010). Therefore the disposal of waste polymers is a serious environmental problem against which public is becoming more aware. The interest of waste polymeric materials disposal is focused on new uses rather than land filling or incineration.

Regarding scrap tires, a strong attention has been paid over last years to the claims for their recycling or reprocessing. In consideration of their complex composition, slow degradation rate in landfill, high calorific value and shape hindrance they may be burned hardly but otherwise they cannot send to landfill anymore and an alternative methodology must be eligible in order to dispose scrap tires. European Directive No. 31/1999 states that the disposal of scrap tires in landfills is banned with the exclusion of bicycle tires and tires with an external diameter greater than 1400mm. Since July 2006 the ban has been extended also to shredded tires.

Waste plastics and tires are very attractive as a source of renewed raw materials and chemical substances. These products may be achieved by pyrolysis, heating usually in the absence, but sometimes in the presence, of an oxidative agent, and these processes may be viewed as a promising technology.

The pyrolysis of polymeric materials or plastic-containing wastes including scrap tires is a possible answer to the problem of their disposal because it let recover of gas, oil and solid able to be employed as a source of products and energy. Therefore the relevance of the pyrolysis processes of plastic waste has been growing.

A plethora of studies over the thermal degradation of polymeric materials are carried out using conventional heating method with internal or external heating source, under inert or oxidizing atmosphere. Generally the thermal decomposition needs operating temperature above 450°C (Kaminsky et al., 2004; Mastral et al., 2002; Whesterhout et al., 1998).

In this area also the interest to microwave heating technologies has become remarkable since they could represent a charming alternative to current technologies based on other conventional heating processes. Microwave heating provides a number of advantages with respect conventional heating methods, mainly referred to the rate and distribution of the heating. It is commonly thought that many limitations should occur nevertheless when switching microwave technology from a laboratory or pilot-scale process to a large scale plant. These limitations mainly concern the lack of data on raw materials amenability with microwave heating and therefore a proper set up of the experimental parameters of the process. The main differences occurring between conventional and microwave heating are shown in Table 1.

Conventional Heating	Microwave heating
Long reaction time (hours)	Short reaction time (minutes)
Hard transfer of heat, thermal conductivity of polymer is low	The low thermal conductivity of polymers may be overwhelmed, easy heating of polymers.
Heating efficiency is hardly obtained	High heating efficiency
Every fuel source may be employed	Electrical power is required
Additive are not required	Microwave absorber are required

Table 1. Comparison between conventional and microwave heating technologies for pyrolysis of plastics.

In this chapter we report the state of art gathered from the scientific literature and patents in addition to our experience and results, concerning the pyrolysis process with microwave heating of polymers and complex plastics. Emphasis will be given to the influence of the main process variables on products obtained: apparatus set-up, temperature, heating rate, microwave absorber and so on. Strong attention will be devoted to the pyrolysis of scrap tires. Tires, due to their high carbon content (up to 30%) are suitable for direct microwave pyrolysis. They are able to absorb microwave and quickly turning it to heat (Meredith, 1998).

The chapter consists of two main sections. The first part is exclusively dedicated to microwave pyrolysis of tires. We report a review of literature and patents, we discuss the results on the bases of our own experience and we integrate them together with our recent achievements in this field. Within the products the liquid fraction is the most attractive due to its high content of valuable hydrocarbons like: benzene, toluene, xylenes and limonene. We thoroughly deal with the relation between layout technologies, operating parameters and products composition. We address in detail the problem to maximize the amount of liquid fraction and valuable hydrocarbons.

The second section is focused on a review of microwave heating pyrolysis of plastic materials. These polymers don't absorb microwave and in order to carry out the pyrolysis is necessary to mix them with a microwave absorbent. Typical absorbent are: coal or carbon-containing materials (for instance tires), metals (Hussain et al., 2010) or metal-oxide (Horikoshi et al., 2009). We report about microwave pyrolysis of the main waste polymeric materials avoiding to send them to landfill (Kaminsky, 1992): polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and polyvinylchloride (PVC). We present the processes proposed and the operative

parameters employed in order to obtain renewed raw materials, refinery feedstock or energy source.

2. Tires pyrolysis

2.1 Why tires pyrolysis?

Usually the recycling policy try to maximize the recovery of materials and minimize the loss of material and energy stored up in wastes (Natural Resources Defense Council [NRDC], 2008). End life tire can be reused for reconstruction processes which magnify the material and energy recovery. However this procedure is limited by quality of waste tires, their deterioration and can be repeated no more than one or two times. Where reuse and remanufacturing are not possible, scrap tires, whole or chopped, 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) and sports (football pitches in synthetic grass and sports flooring for athletic tracks).

Sure enough not the whole production of scrap tires can be reprocessed or reused indeed 19% of them is disposed in Italy with heat treatment processes mainly for the recovery of energy content (FISE UNIRE, 2009). The main technological processes available for heat treatments are listed below:

- incinerator (including municipal solid waste incinerators) (Sharma et al., 2000);
- fuel for rotary kilns or furnaces to produce cement or steam (Giugliano et al.; 1999);
- pyrolysis.

Just the last process mentioned, the pyrolysis, has the characteristics to transform waste polymeric materials in products suitable for energy production or petrochemical feedstock.

2.2 Microwave or non-microwave heating in pyrolysis processes: two different approaches

Pyrolysis is a thermal cracking process performed in inert atmosphere, such as nitrogen, helium or CO₂, and let to the total recovery of mass as a solid (non-volatile material), liquid (condensable fraction) and gaseous (non-condensable fraction) products (Kaminsky, 2006). These three products are always obtained regardless the apparatus, heating source, operating temperature and heating speed. The aim in all research is usually to enhance yields in liquid product and to control products characteristics. The pyrolysis is an endothermic process, typical energy consumption 4.0-5.7 MJ Kg⁻¹ (Piskorz et al., 1999), and the thermal energy required could be provided in several ways resembled in two main categories: conventional and non-conventional.

Conventional heating included heating sources internal (partial combustion of the load for instance) or external to the reactor: electrical resistance (Burrueco et al., 2005), flame (Williams et al., 1998) or microwave (Ludlow-Palafox & Chase, 2001). Among non-conventional heating may be included also plasma (Tang & Huang, 2004) and supercritical fluids (Chen et al., 1995). Up to now a wide number of apparatus and reaction conditions were experimented for conventional, non-microwave, heating pyrolysis. Alternative to this technology is microwave pyrolysis.

Only the pyrolysis process with conventional (external or internal) heating are up to now for large scale applications the only one employed.

Any apparatus, besides autoclave, is composed of few main parts: reactor, heat production and exchanger, collecting system.

The fundamental part of any apparatus is the reactor, where the heat is transferred from the source to the material. Many type of reactors are available, here are listed only the main classes: autoclave (de Marco Rodriguez et al., 2001), rotary kiln (Li et al., 2004), static bed reactor (Cunliffe & Williams, 1998; Burrueco et al., 2005) and fluidized bed reactor (Kaminsky & Mennerich, 2001, Aylòn et al., 2008; Aylòn et al., 2010). Their feature and main operating parameters are reported and compared in table 2.

Reactor Type	Temperature range (°C)	Heating Rate (°C min ⁻¹)	Main Feature
Autoclave	300-700	15	Products don't vent, poor thermal transfer
Rotary kiln	450-650	-	Fixed speed feeding, heat transfer improved by lowering tire size
Static bed reactor	400-700	5-12	Long reaction time, products vent from reactor
Fluidized bed reactor	500-600	-	Continuous process, optimal thermal transfer

Table 2. Reactor employed in non-microwave pyrolysis: main features, operating temperature and heating rate.

In table 2 are also underlined the temperature range and heating rate tested. The temperature and the heating speed are parameters of paramount importance and together with apparatus affect the products composition. In order to simplify the approach we focus just on these three process variables. Other variables such as load size, apparatus set-up, pyrolysis running time and material flux inside the reactor are discussed afterwards.

The choice of one of these reactors is linked with two aims: effectiveness and manageable transfer of heat to the polymeric material and volatilize products from the reactor towards collecting system. It is essential an efficient heat transfer due to the poor thermal conductivity of tires and polymeric material. The possibility to control the heat transfer is fundamental to obtain uniform products.

Without taking care of the others variables just the fluidized bed reactor fulfills all the above requirements. The heating medium is usually quartz sand preheated and kept at the prefixed temperature while the polymeric material is continuously fed (Kaminsky & Mennerich, 2001). Nevertheless the process is sensitive to fibers and high amounts of metals and fillers (Kaminsky et al., 2004). It requires high operating cost for heating and complex feedstock preparation making this kind of reactor relatively expensive (Juma et al., 2006). For instance Kaminsky use 9 kg of quartz sand to treat up to 4 kg of chopped polymers (Kaminsky & Mennerich, 2001).

On the other side a simpler approach is possible when working with static bed reactor or autoclave in a batch process. The reactor is just heated together with the polymer to the required temperature. It is kept to this temperature until the end of the experiment (Cunliffe & Williams, 1998; Mastral et al., 2000; González et al., 2001; Burrueco et al., 2005). Anyway the heat transfer is not effective in this type of reactors and it can be improved by upgrading

the reactor with a continuous mixing of the load or with a spinning movement that is a rotary kiln (Li et al., 2004).

The heating rate and final temperature affect the properties and yields of the three products. It is deeply described in paragraph 2.3. Anyway different reactors may give different products even if the final or operating temperature is the same in each reactor.

An improving of the reactor technologies to effectively transfer the heat requires a control over the load size. A static bed reactor, autoclave, or rotary kiln doesn't need any particular load size, just small enough to be filled during the experiments. In the fluidized bed reactor usually a size of 1-2 mm (Kaminsky & Mennerich, 2001), 2 mm (Aylón et al., 2008) or no more than 5 mm (Aylón et al., 2010) is required.

The limitations displayed above are held back controlling the other experiment's variables: pyrolysis running time, apparatus set-up and material flux. Where a good heat transfer is achieved shorter reaction time is required. Kaminsky reports 230 minutes to pyrolyze 4 kg with its fluidized bed reactor (Kaminsky & Mennerich, 2001) while Berruenco's process requires up to 300 minutes to pyrolyze 0.3 kg with its static-bed reactor (Berruenco et al., 2005).

Another way to overwhelm the not optimal heat transfer is the control of the flux of material and consequently the apparatus set up. Except for autoclave, where all the products are forced inside the reactor, all the others described reactors require a gas circulating system to remove the pyrolyzed products at the desired time.

Again a longer residence time of the volatilized products is used when the heat transfer is not optimal and it lets a more efficient cracking. Static-bed reactor requires up to 120 s of residence time of the gas in the reactor and this is achieved by a controlled nitrogen flux (Berruenco et al., 2005) or apparatus set-up (Cunliffe & Williams, 1998). The residence time of the gas in the fluidized-bed reactor is less than 3 s and it is achieved with strong flux of nitrogen or other inert gas (Kaminsky & Mennerich, 2001).

This description of main reactor technologies available is far away to be exhaustive; it wants only to give an idea of the possible approaches to the pyrolysis of tires and plastics.

When we switch to a microwave heating system the apparatus set up is almost the same: efficiently and manageable transfer of heat to obtain products with desired proprieties. Only the reactor is the feature which must be changed.

The scientific literature is extremely poor with respect to the patent literature. Unfortunately for scientific spread the patents don't give extensive information concerning the products achievable by the described apparatus. Anyway it is possible to understand the approach to the microwave pyrolysis of tire and plastics.

The goal in each patent is to provide a simple and economically convenient approach to the pyrolysis of both tires and plastics. It is achieved by treating the polymeric substrate in a static bed-type reactor. Holland (Holland, 1995) uses a static-bed reactor filled with carbonaceous materials (tires or coal) between 400 °C and 800°C to pyrolyze any kind of polymers. More recent patents showing similar approach, which always resemble a static bed reactor, are reported by many authors (Holland, 1992; Parker, 1992; Johnson et al., 1996; Pringle, 2006; Pringle, 2007; Kasin, 2009). Just the feeding system and the reactor design diversify the several patents. They are planned to be employed for industrial application. Strong attention is paid to productivity and energy efficiency.

Recently a more complete microwave pyrolysis plant was proposed from Scandinavian Biofuel Company (Scandinavian Biofuel Company [SBC], 2011). All the products were evaluated as source of electric energy and after subtraction of the energy required for the

process give a production of 1.55 MWh/ton from tires or 3.98 MWh/1 ton from plastics. The hypothetical working capacity for SBC plant is reported in table 3.

Feedstock	Plastics	Tires
Capacity/yr	25,000 tons	25,000 tons
Water Content	5%	1%
Net capacity/yr	25,000 tons	20,000 tons
Output oil	12,500 tons	5,600 tons
Output gas	10,000 tons	3,000 tons
Output carbon	1,200 tons	11,000 tons
Electricity output	103.4 GWh	44.5 GWh
Electricity use	3.79 GWh	4.57 GWh
Electricity sales	99.65 GWh	39.89 GWh

Table 3. Project examples for electricity production from SBC plant.

From the few scientific articles available up to now for microwave pyrolysis of polymeric materials two kind of apparatus came out: static bed batch reactor (Hussain et al., 2010) and fluidized bed reactor (Ludlow-Palafox & Chase, 2001).

The static bed reactor used by Hussain et al. is as simple as possible. The microwave absorbent is an iron mesh mixed with the polymer (just polystyrene in this article). The products are collected by two cold traps.

Ludlow-Palafox & Chase use a reactor resembling the fluidized bed reactor of Kaminsky, where the heat carrier is carbon instead of quartz sand (Kaminisky & Mannerich, 2001). The temperature is risen up and kept to the prefixed temperature before adding the polymers. Small amount of polymers is dropped at time intervals directly into the reactor, 50g of polymers for 1000g of heated carbon, to prevent large temperature fluctuation. It is required a small amount of time (120 s) to complete the pyrolysis in these conditions. Anyway with this productivity to pyrolyze 4 kg, as reported by Kaminsky & Mannerich with their fluidized bed reactor, is possible to extrapolate a reaction time of 120 minutes instead of 230 minutes for fluidized bed reactor. There’s a huge difference. Furthermore the full potentiality of microwave oven is not used.

In our experiments we use a static bed reactor approach in a batch process to simplify most of the apparatus and to minimize the energy consumption.

The system is composed by a microwave oven, a heat exchanging pipes and collecting flasks. The volatilized material is moved towards the condensing traps by the products formed in the course of the pyrolysis and the partial condensation of gases. In this way the gases vented out are not diluted by transport gas. Up to now the experiments were carried out by heating the chopped tires and plastics from room temperature to the complete pyrolysis of material. The pyrolysis starts usually 20 seconds after switching on microwave. The experiments are conducted using an increasing microwave power. In this way only the energy necessary for the pyrolysis itself is supplied inside the oven.

In the best conditions tested until now we are able to pyrolyze 0.4 Kg of tires in 14 minutes. Here is possible to extrapolate 140 minutes for 4 kg of tires. It is a big improvement from the static bed reactor and slightly better than fluidized bed reactor from Ludlow-Palafox & Chase. Also in this case the full potential of the microwave oven is not used.

2.2.1 The problem of high temperature measurement when switching on microwave

When the microwave is not employed the temperature is easily measured by thermocouples. When microwave is turned on a metal thermocouple can't be used anymore. It absorbs the microwave radiation and provides a skewed temperature. Up to now are available two technological solutions to investigate the high temperature during the microwave pyrolysis process: infrared and fiber optic thermometer. The infrared thermometer is a contactless thermometer which can work properly in a wide range of temperature. It measures the radiation emitted in the infrared region of the spectrum which is linked to the temperature. It consists in a lens to focus the infrared energy onto the detector which converts the energy to an electric signal that may be displayed in units of temperature after calibration. The main limitations of this instrument are its calibration and the medium value of the temperature of objects present. It is available at a relatively low price. The common fiber optic thermometer commercially available is not suited for high temperature detection. They can be used in a temperature range up to 400°C, over this temperature they melt. A quite new technology in optic fiber is now accessible based on sapphire crystalline fiber (Djeu, 2000). It can work up to temperature of 950°C, and it is perfectly suitable for temperature detection in a microwave pyrolysis experiment (Micromaterials Inc., 2010). The main advantage of this fiber optic probe is the detection of temperature in a single position where the probe is placed. The infrared thermometer on the other side averages the temperature over a large area and this could lead significant errors. We have to remember that the heating is not homogeneously distributed but localized on the microwave absorbent that are mixed with the polymeric materials.

2.3 Conventional tires pyrolysis: products characteristics

The three products, solid, liquid and gas, have been fully characterized and the results reported in many papers on non-microwave pyrolysis. Due to this reason it is really interesting to review them for a better understanding of microwave influence on products characteristics. Tires have a variable composition, depending on brand, dimensions and use. In tables 4 and 5 are reported the average composition of truck and car tires (Rubber Manufacturers Association [RMA], 2011).

Tires for	Polisoprene 1,4-cis (wt%)	Synthetic Polymers (wt%)	Carbon Black (wt%)	Steel (wt%)	Sulfur (wt%)	Textile, additive (wt%)
Car	14	27	28	14-15	1.5	16-17
Truck	27	14	28	14-15	2.5	16-17

Table 4. Average composition of truck and car tires. Synthetic polymers include: polybutadiene (BR, butadien rubber), styrene-butadiene copolymers (SBR, styrene-butadiene rubber) and EPDM rubber (ethylene propylene diene Monomer (M-class) rubber).

Even if tire composition is variable, yields obtained from the pyrolysis are not strongly affected by it (Kyari et al., 2005). Variation in products characteristics are appreciated only

when significant differences between tires occurred. Their characteristics are mainly affected by temperature, heating speed and feeding size as reported in paragraph 2.2.

Element	%
C	80.1
H	7.0
N	0.4
S	1.5
O	3.0
Ash	8.0

Table 5. Average elemental composition (CHNSO) of tires.

The main gas components are: H₂, H₂S, CO, CO₂, CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and other organic substances in lower amount. It has a high gross calorific value of 68-84 MJ m⁻³ (de Marco Rodriguez et al., 2001) when it is rich in hydrocarbons and a lower one, 30-40 MJ m⁻³ (Williams et al., 1990), when depleted in organic compounds. It may be used as an energy source for sustaining the pyrolysis process itself (Williams et al. 1998; Kyari et al., 2005).

The liquid, or pyrolysis oil, is the most scientific and economical interesting product due to its high gross calorific value and content of valuable hydrocarbons such as: benzene, toluene, xylenes, limonene and so on. It can be employed as energy source, refinery feedstock or reservoir for aromatics and limonene (Laresgoiti et al., 2004).

The solid is mainly made of carbon and non volatilizable material: steel and inorganic additives (de Marco Rodriguez et al., 2001). The steel can be easily removed with electro-magnets. The carbonaceous fraction is employed up to now as fillers in tires manufacturing (de Marco Rodriguez et al., 2001), activated carbon production (Mui et al., 2004) and smokeless fuel (Diez et al., 2004).

The yields for the three products are strictly connected with the process variables as introduced in paragraph 2.2.

In table 6 the yields obtained by various authors in different reaction conditions are reported.

A comparative study is not easy to carry out. The data reported in table 5 are not congruent among them due to the different reactors and conditions employed. Anyway a trend in all of them may be easily obtained. There's a critical temperature above which the pyrolysis is completed and the solid yield doesn't significative change. In any study it is around 500°C.

When the temperature is rising over 500°C, while the solid product remain almost constant, the yield of liquid product goes down due a stronger cracking which improve the yield of non-condensable fraction.

The yield of liquid is lower when the residence time of liquid in the oven increase. The autoclave, where the pyrolysis products don't vent out, the yield of non-condensable fraction is three times higher than the one achieved in a static bed reactor. In a fluidized bed reactor with a residence time of 3 seconds gives similar gas yield than a static bed reactor where the residence time is 120 seconds. When the reaction time increases the cracking of liquid products remarkable rises up to 3 times.

Author	Max Temp (°C)	Heating speed (°C/min)	Running time (min)	Yields			Comments
				S	L	G	
Burreco et al., 2005	400	NA	240	64.0	30.0	2.4	Static-bed batch reactor
	500	NA	240	52.7	39.9	3.6	
	550	NA	240	52.5	39.1	3.6	
	700	NA	240	51.3	42.8	4.4	
de Marco Rodriguez et al., 2001	400	15	55*	55.9	24.8	19.3	Autoclave
	500	15	62*	44.8	38.0	17.2	
	600	15	68*	44.2	38.2	17.5	
	700	15	75*	43.7	38.5	17.8	
González et al., 2001	400	-	30	55.1	42.9	2.0	Static-bed batch reactor, sample 4g.
	500	-	30	38.6	55.4	6.0	
	600	-	30	37.0	52.2	10.8	
	700	-	30	36.7	36.6	26.7	
Aylón et al., 2010	600	-	NA	40.6	41.5	17.9	Moving bed reactor, without steel
	700	-	NA	39.0	31.3	29.7	
	800	-	NA	41.0	27.5	31.5	
Kaminsky & Mannerich, 2001	500	-	230	30	65	5	Moving bed reactor, tires composition simulate
	550	-	220	34	57	9	
	600	-	240	40	51	9	
Cunliffe & Williams, 1998	450	5	150	37.4	58.1	4.5	Static-bed batch reactor, load pre-heated at 150°C
	500	5	160	38.3	56.2	5.5	
	560	5	172	38.1	55.4	6.5	
	600	5	180	38.0	53.1	8.9	
Li et al., 2004	450	-	200-250	43.9	43.0	13.1	Rotary kiln, 50 kg processed
	500	-	200-250	41.3	45.1	13.6	
	550	-	200-250	39.9	44.6	15.5	
	600	-	200-250	39.3	42.7	18.0	

Table 6. Yields and parameters of non-microwave tires pyrolysis reported by various authors. S: solid; L: liquid; G: gas. *Estimated. NA: not available.

2.3.1 Non-condensable fraction (gas)

Each apparatus is provided with a condensation system, in order to collect the liquid products. In order to maximize the yield of the liquid products different heat exchanging systems were tested and this is an extra variable affecting the gas composition in each report.

However the non-condensable fraction contains permanent gas (such as: H₂, H₂S, CO, CO₂ and CH₄) and organic substances with high vapor pressure difficult to condensate.

In table 7 is summarized the amount of the main compounds identified in each gaseous mixture reported by various authors.

Author	Max Temp (°C)	Compound (vol. %)									
		H ₂	CO _x	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃	C ₄	C ₅	C ₆	H ₂ S
Burreco et al., 2005	400	2.6	2.5	1.0	0.4	0.3	0.5	3.2	0.0	0.3	-
	500	14.2	1.3	4.3	1.5	0.7	1.3	2.3	0.0	0.4	-
	550	17.9	1.1	5.6	1.8	0.8	1.5	2.0	0.0	0.3	-
	700	10.1	1.6	5.4	1.6	1.2	1.6	2.5	0.0	0.5	-
de Marco Rodriguez et al., 2001	400	-	14.9	4.4	4.5	4.3	8.5	36.9	16.5	7.3	2.6
	500	-	14.2	19.8	9.1	9.4	10.8	21.3	7.6	2.8	5.1
	600	-	15.3	20.0	9.0	9.7	10.6	21.9	7.4	2.5	3.6
	700	-	21.8	20.6	8.1	8.9	7.7	19.8	6.7	2.5	3.9
González et al., 2001*	400	36.7	50.6	12.7	0.0	0.0	-	-	-	-	-
	500	19.8	34.4	22.9	15.3	7.6	-	-	-	-	-
	600	16.5	20.4	28.5	28.5	6.1	-	-	-	-	-
	700	18.7	7.1	34.7	32.5	7.1	-	-	-	-	-
Kaminsky & Mannerich, 2001 **	500	0.1	12.5	3.0	4.6	3.1	10.5	63.2	-	-	3.0
	550	0.2	7.5	3.8	5.4	5.1	13.7	62.5	-	-	1.8
	600	0.2	8.7	4.1	5.1	8.0	16.4	55.2	-	-	2.2
Díez et al., 2004	350	24	3.3	20	29		12	5.7	3	1	-
	450	30	3.0	24	26		9	4.3	2	0.2	-
	550	40	3.0	26	20		6	2.8	1.1	0.1	-

Table 7. Main compounds present in the gas. * Values are extrapolated (Pressure of 25 atm) where they are reported as mol kg⁻¹ of scrap tire. ** Values are calculated where are expressed as mass percentage.

The inorganic substances, H₂S, CO_x and H₂, are connected to three tire components. The sulfur compounds come from the vulcanization process of the polymeric tire constituents. A variable amount of sulfur is used to improve the rubber elasticity. In the gases only hydrogen sulfide is found as sulfur containing compound, any organic sulfur containing products are not found. Carbon dioxide and carbon monoxide find their origin from two sources: metal carbonates and oxygen containing inorganic substances. Both of them are additives in tire formulation. Hydrogen is a common cracking product. What happen in a pyrolysis reactor is close to a thermal cracking in a petroleum refinery. The organic substances find their origin from the random cracking of polymers. The growing presence of olefin instead of their paraffinic equivalents is linked to a working temperature in the range 400-700°C where alkenes are thermodynamically more stable than alkane.

2.3.2 Condensable fraction (liquid)

The condensable fraction, also known as liquid fraction or pyrolysis oil, is the most interesting and studied product. The maximum yield is obtained working with a pyrolysis temperature between 450 and 550 °C as shown in table 5, it varies between 30% and 58% depending if steel cords are considered in calculation. Its color is dull dark-brown and it has a bad-smelling flavor. It has a complex composition which is usually studied using a gas

chromatograph coupled with a mass detector. An enormous amount of substances are identified, more than 300, but only few compounds are present in an amount greater than 1% (Laresgoiti et al., 2004).

In table 8 are reported the top 12 substances identified inside the condensable fraction from some authors.

Author	Max T (°C)	Compound											
		Benzene	Toluene	Ethylbenzene	Xylenes	Styrene	2-Ethyltoluene	α -methyl styrene	Limonene	1H-Indene	Naphthalene	Benzothiazole	1,6-dimethyl naphthalene
Laresgaoiti et al., 2004	400	0.65	1.00	1.07	0.69	0.36	0.15	3.22	0.17	0.18	0.53	0.25	0.65
	500	0.94	1.00	1.25	0.88	0.40	0.11	1.84	0.32	0.26	0.33	0.30	0.94
	600	2.34	1.00	1.09	1.03	0.16	0.11	1.70	0.34	0.34	0.39	0.36	2.34
	700	1.46	1.00	1.33	1.01	0.50	1.26	2.30	0.42	0.41	0.53	0.50	1.46
de Marco Rodriguez et al., 2001*	400	-	-	-	-	-	-	-	-	-	-	2.10	-
	500	-	-	-	-	-	-	-	-	-	-	1.80	-
	600	-	-	-	-	-	-	-	-	-	-	2.00	-
	700	-	-	-	-	-	-	-	-	-	-	1.80	-
Kyari et al., 2005*	500	0.85	1.00	0.11	0.52	1.91	0.27	3.34	0.16	0.05	0.17	0.28	0.85
Kaminsky & Mannerich, 2001	500	0.73	1.00	0.21	1.60	-	0.57	-	0.08	0.07	0.60	-	0.73
	550	1.00	1.00	0.38	0.87	-	0.37	-	0.09	0.08	0.40	-	1.00
	600	1.24	1.00	0.32	1.82	-	0.44	-	0.18	0.15	0.21	-	1.24

Table 8. The 12 main substances present in the liquid fraction. The data reported are normalized to toluene. * It is the percentage over total liquid fraction.

The liquid fraction is a mixture of organic compounds from C₄ to C₂₄, mainly olefins, single ring aromatics and limonene. Within the minor substances strong attention should be devoted to three classes of compounds always present: polycyclic aromatics hydrocarbons (PAHs), sulfur containing products and other heteroatoms containing substances.

In figures 1-4 are reported the mechanism proposed for the degradation of polymeric materials (Cunliffe & Williams, 1998; Mastral et al., 2000).

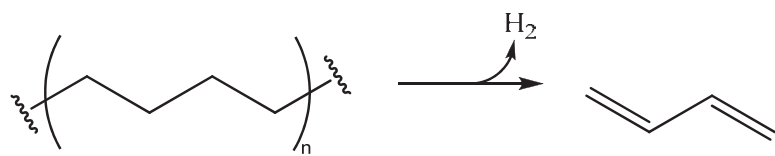


Fig. 1 Cracking of linear polyolefins.

Element	Abundance (wt%)
C	71.5
O	13.3
Fe	5.4
S	2.8
Zn	2.3
Ca	1.3
Al	0.3

Table 9. Elemental composition of a non-volatile fraction (solid).

The steel cords are not scratched at pyrolysis temperature and they may be separated by an electromagnet. The remaining solid product is investigated and may be employed as active carbon in grain or pellets (Mui et al., 2004; Pantea et al., 2003). It is obtained by treating the raw carbonaceous non-volatile product at temperature between 800°C and 1000°C in the presence of an activating agent such as H₂O or CO₂. The active carbon obtained in this way has high active surface similar to the commercial product.

The carbon may be used as sorbent for organics (phenols and colorants), metals, chlorinated compounds and gases (butane for instance). Anyway the polluting metals present inside the active carbon (Cr, Cd) may be released and any application must be accurately monitored. Carbon may be also employed as a source of energy by combustion process.

2.4 Microwave tires pyrolysis

Up to now the microwave pyrolysis are exploited in laboratory and pilot plant scale. Anyway the greatest difference, if correlated to thermal heating, dwells in uniform and efficient heating. We carry out experiments using a microwave oven that assure uniform distribution of the microwaves inside the chamber and equipped with the possibility to control the power of microwave supply. In this way it is possible to modulate the speed of thermal degradation and the yield of products together with their characteristics.

Yields of the liquids are in the range between 37-40%, similar to those reported for non-microwave pyrolysis (steel cords are counted) when the optimal conditions are achieved, otherwise fewer yields are obtained.

In table 10 are listed the yield of five representative experiments.

MW power (kW)	Time (min)	Solid (wt%)	Liquid (wt%)	Gas (wt%)
6	13	50.10	26.72	23.18
3	39	50.45	37.21	12.34
1.5	100	69.38	18.09	12.53
1.5 to 4.5	76	49.65	38.76	11.59
1.5 to 6	59	48.36	36.35	15.29

Table 10. Microwave pyrolysis: correlation among power, time and yields.

The cracking is already effective when half of the maximum power is employed. If the power is lower than 1.5 kW, in our oven, it is not possible to complete the pyrolysis itself. Anyway the properties of collected products vary amazingly.

The properties of non-volatile fraction anyway are slightly affected by the microwave power and the product has close characteristics to that one obtained from a non-microwave oven.

The composition of non-condensable organic fraction changes as function of microwave power and the results are summarized in table 11.

Substance	MW power (kW)				
	6	3	1.5	1.5 to 4.5	1.5 to 6
Hydrocarbons C1 + C2	46.54	76.79	70.29	27.39	29.22
Hydrocarbons C4	25.29	11.60	17.30	40.44	38.26
Hydrocarbons C5	1.20	0.75	0.94	1.79	2.07
2-methylbutadiene	10.23	3.60	5.18	-	10.88

Table 11. Main substances identified in non-condensable product.

High microwave power increases the production of volatile materials which flow quickly out of the reactor and they are not subsequently cracked. A slow heating is not good enough to break the gaseous molecules while a mid-power heating is suited to crack the polymers macromolecules and let them to stay for a long time in the reactor to be degraded to simple molecules such as methane, ethane and ethene. Minor amount of organic sulfur containing substances like ethylene sulfide are present in gases.

Among inorganic substances remarkable is the presence of H₂ which rises up to 36% when the microwave power is 3 kW. This result is not easy comparable with non-microwave results: just in few experiments where the residence time of gases inside the reactor is long similar results are achieved.

The condensable fraction (liquid) is deeply affected by microwave power. Its appearance switches from a dark dull liquid when the full power is used to a yellow clear solution when 1.5 kW is used. Decreasing the power also the viscosity is lower.

Anyway the GC/MS analysis gives a better idea how much the liquid product changes its properties.

The main substances identified and their relative abundances are reported in table 12.

Compound	Abundance %				
	6 (kW)	3 (kW)	1.5 (kW)	1.5to4.5 (kW)	1.5to6 (kW)
2-butene	1.63	1.49	1.05	1.21	0.81
1,3-pentadiene	3.18	1.63	1.49	1.70	0.31
3-methyl-1-esene	2.09	1.57	1.40	1.63	0.64
Benzene	3.91	1.71	2.78	2.26	1.66
Toluene	4.55	2.87	3.52	3.11	2.51
Xylenes	6.92	5.22	7.48	7.08	3.43
Styrene	3.06	1.39	1.45	1.85	0.76
Trimethylbenzenes	3.23	3.03	4.57	4.54	2.53
α-methylstyrene	0.62	0.39	-	1.33	0.24
1-ethyl-3-methylbenzene	0.99	1.01	1.27	1.41	0.78
1,2,4,5-tetramethylbenzene	0.76	1.40	2.10	2.41	1.19
Limonene	3.72	3.43	2.49	3.49	0.82
1H-Indene	0.87	0.38	0.28	0.50	0.46
Naphthalene	0.97	0.43	-	0.20	0.77
Benzothiazole	0.59	0.57	0.25	0.32	0.58

Table 12. Main substances in liquid product, obtained using different microwave power.

A fast pyrolysis with a power of 6 kW yields a huge amount of aromatics (up to 20%). Decreasing the microwave power the aromatic yield decreases. Probably the microwave energy is not enough to perform dehydrogenation reactions.

The reduction of microwave power leads a change in other properties of liquid such as: viscosity, density and fraction of distilled product.

Viscosity and density are directly connected with microwave power. The density changes among 0.800 g cm⁻³ and 0.900 g cm⁻³, while the viscosity is in the range 0.7 – 2.6 cPs.

The fraction of product distilling at temperature lower than 210°C changes deeply when the power is lowered as shown in table 13.

MW Power (kW)	Distillate under 210°C (%)
6	22.93
3	37.61
1.5	74.61

Table 13. The distillation of condensable fraction. Only the amount of distillate under 210°C is reported.

The trend is almost linear and interesting results are achieved. In non-microwave pyrolysis only 20% of liquid fraction is distillable under 210°C.

Using a microwave heating is possible to manage properly the yields and proprieties of condensable and non-condensable products.

3. Microwave pyrolysis of polymeric materials

As well as tires pyrolysis the microwave pyrolysis of single polymeric materials has been investigated by many authors (Kaminsky & Zorriqueta, 2007; Arandes et al., 2008; Kim, 2001; Yoshioka et al., 2004; de la Puente et al., 1998). Five main categories of polymers were tested: polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and polyvinylchloride (PVC). All of these polymers are not able to absorb microwave and turn it into heat. So a microwave absorbent must be employed to carry out the pyrolysis, as reported in a previous paragraph. Carbon powder (to avoid unwanted interference) or chopped tires has been employed as microwave absorbent.

The microwave influence on the products yields is poor but it is strong on the properties of liquid fraction and this influence is reported in the following paragraphs.

The non-microwave pyrolysis of the above mentioned polymers has been deeply studied and characterized. In the first instance the microwave pyrolysis seemed to be more suited for multi materials pyrolysis such as: Tetra Pak® or laminates (Ludlow-Palafox & Chase, 2001).

Usually the pyrolysis of a pure plastic material yields just a liquid and a gas product. In few experiments is reported the growing up of a solid product and usually low attention has been paid to this aspect. In our apparatus a low amount of non-volatilized fraction is always found when the polymers are pyrolyzed in the presence of coal, presumably due to a strong localized heating. In table 14 are listed some experiments with relative yields for the pyrolysis of single plastics.

MW power range (kW)	Polymer	Time (min)	Absorbent-polymer ratio	Solid (wt%)	Liquid (wt%)	Gas (wt%)
1.8 to 3*	HDPE	33	2:1	42.49	44.98	12.09
3	HDPE	75	1:2	0.40	83.92	15.68
1.2 to 6*	HDPE	265	2:1	35.52	45.83	18.65
1.8 to 3*	PP	39	2:1	35.29	54.00	10.72
3	PP	68	1:2	15.89	70.82	13.29
1.8 to 3*	PVC	71	2:1	53.16	17.70	29.14
1.8 to 3	PVC	47	1:1	13.92	10.25	75.83
3	PVC	21	1:2	14.69	3.44	81.87
1.8 to 3*	PET	40	2.5:1	38.20	35.32	26.48
1.2 to 3*	PET	207	4.2:1	48.29	26.34	31.99
3 to 6	PS	59	1:2	6.83	89.25	8.92

Table 14. Microwave pyrolysis: correlation between microwave power and yield. * Tires instead of coal as microwave absorber.

3.1 PE microwave pyrolysis: products characteristics

The polyethylene (PE) is the most important and used plastic. It is a thermoplastic polymer, chemically inert and is used in an enormous range of applications. It is produced as a linear High Density (HDPE) or a branched Low Density (LDPE) polyethylene.

The thermal degradation of HDPE starts over 380°C (Bockhorn et al., 1998). When HDPE is heated to a temperature below 730°C it forms mainly a wax (a semi-solid product) and a liquid. Together with the increasing of the temperature the amount of wax decreases in advantages to liquid and gas products. At 730°C there is no further formation of wax, just liquid and gas (Mastral et al., 2002). Over 800°C the conversion of the polymer in gases is almost total: 91.2% at 850°C (Westerhout et al., 1998).

The cracking of the polymers chain leads to a large distribution of numerous linear hydrocarbons having different length. This distribution is a function of microwave power and working temperature. At high cracking temperature the product is liquid at room temperature otherwise it is solid.

The gas is composed of H₂, CH₄, C₂H₆, C₂H₄, C₃H₈, and C₃H₆. The liquid and wax are made of alkanes, from C₁₁ to C₅₇, and their equivalent 1-alkene and 1,3-dialkene (Williams & Williams, 1999a).

Anyway too high temperature causes the formation of aromatics with the reaction path proposed in figure 3. Together with high temperature also long residence time promotes the formation of aromatic compounds.

The pyrolysis of HDPE using microwave heating requires HDPE flakes mixed with a microwave absorbent such as coal or chopped tires. Different microwave power gives completely different products. In table 14 are listed the yields in solid, liquid and gas using different microwave power and absorber.

When microwave power of 3 kW is used a wax is largely produced and the amount of a liquid product inside the wax for analysis is hardly recovered. Anyway when milder reaction conditions are used, lowering the microwave power, a liquid product is collected. It has been obtained using 1.8 - 1.2 kW, but in this condition it is not possible to complete the pyrolysis without the erogation of a higher power of microwave in a subsequent step. By the

simple modulation of the microwave power is not possible to obtain, without other treatments or apparatus, only a liquid product.

The liquid fraction, analyzed via GC/MS, contains linear saturated hydrocarbons and their terminal unsaturated equivalent from C₆ to C₃₂.

The only way to obtain a liquid product instead of wax is the cracking of the wax in a second reactor, refluxing them again in the pyrolysis reactor or using a catalytic system which resemble a refinery unit (Arandes et al., 2008).

3.2 PP microwave pyrolysis: products characteristics

The polypropylene (PP) is the second most used polyolefin in the world due to the low-cost of monomer production together with flexible properties.

The degradation mechanism yields a chain cracking to a wax and a liquid. They are composed of hydrocarbons from C₁₁ to C₅₇ (Westerhout et al., 1998). Rising the pyrolysis temperature the wax yield decreases. Anyway these conditions lead to the formation of aromatics due to further reactions of hydrocarbons obtained in the first instance (see scheme reported in figure 3).

The PP is more unstable than HDPE to thermal degradation due the presence of a large extent of tertiary carbons giving more stable radicals with respect to primary or secondary radicals formed in the pyrolysis of PE. The pyrolysis of PP may be carried out at 500°C instead of 700°C as required for HDPE (Kaminsky & Zorriquet, 2007)

An analogous effect is shown when the pyrolysis is performed using a microwave oven. The products are liquid at room temperature independent from the microwave power and the microwave absorbent: coal or chopped tires. In table 14 are reported two experiments performed at different microwave power.

The high reactivity of PP leads often to the formation of a solid product.

The liquid fraction contains organic compounds from C₆ to C₃₀. In table 15 are reported the main components identified by GC/MS analysis in the low boiling fraction (below 145°C) of the liquid product obtained using 3 kW as microwave power source.

Compounds	Composition (%)
4-methylheptane	3.78
2,6-dimethyl-2-octene	3.69
1,3,5-trimethylcyclohexane	4.88
3,7-dimethyl-1-octene	57.3
1,2,4-trimethylcyclohexane	5.17
3,5,5-trimethylcyclohexane	3.45
1-nonene	18.93
Total	97.20

Table 15. Main compounds present in the low boiling fraction of the microwave pyrolysis of PP using a power source of 3 kW.

All the substances formed by PP degradation are methyl derivatives. For instance 3,7-dimethyl-1-octene is very close to the repeating unit of PP as shown in figure 5.

Anyway few aromatic substances are present in liquid products when pure PP is pyrolyzed using a microwave oven with respect to the compounds present in a thermal pyrolysis of PP (Kaminsky, 2006). This is connected with a different way of heat transfer. The heat provided by microwave oven is quickly employed to break the polymers avoiding subsequent reactions.

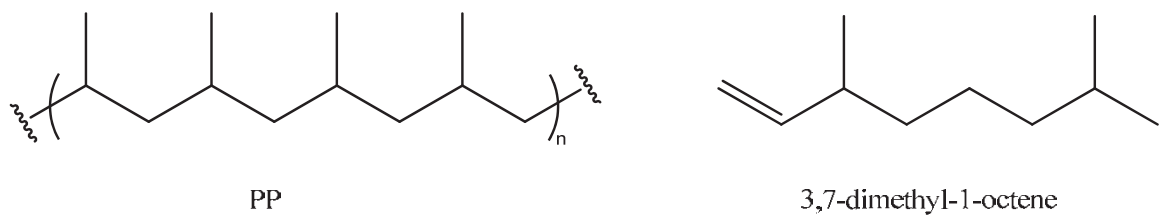


Fig. 5. A molecule formed in the liquid from pyrolysis of PP.

3.3 PVC microwave pyrolysis: products characteristics

The polyvinylchloride (PVC) holds a unique position among commercial polymers. It is cheap and used in a wide range of applications due to its high versatility. Usually it is added with stabilizers, lubricating, plasticizers, fillers and so on. To avoid interference due to large amount of additives present, the microwave pyrolysis of PVC has been carried out on pure PVC. The thermal degradation of PVC takes place in two-steps process: dehydrochlorination followed by residual chain cracking. The elimination of hydrogen chloride from the chain back bone is fast and complete. It happens at temperature among 300°C and 330°C (Bockhorn et al., 1998; Kim, 2001). The reaction scheme is reported in figure 6.

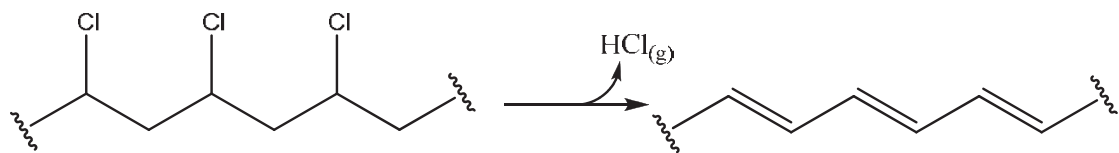


Fig. 6. Dehydrochlorination of PVC.

The gases are mainly composed of HCl, ethylene and propylene. The liquid fraction contains aromatic compounds such as benzene, toluene and styrene (Saeed et al., 2004). The microwave pyrolysis of PVC follows the same two steps of thermal pyrolysis. The polymer quickly eliminates HCl that has been absorbed in NaOH traps after the collecting flasks. Up to 97% of chlorine in PVC chain is found in the traps. Few chlorine organic compounds are present in liquid products. In table 14 are reported the PVC pyrolysis at different microwave power. As reported in the literature for thermal pyrolysis also in the microwave pyrolysis the main products present in liquid fraction are aromatic compounds, the main components of the liquid are listed in table 16.

Compounds	Composition (%)
Benzene	18.56
Toluene	8.73
1,3-dimethyl-benzene	4.25
1,4-dimethyl-benzene	2.49
Styrene	0.46
1,2-dimethyl-benzene	3.44
Naphthalene	4.01
Total	41.94

Table 16. Main aromatic compounds formed in PVC/coal pyrolysis.

The formation of aromatics in high yield may be attributed to Diels-Alder type reactions involving the poly-unsaturated chain formed after dehydrochlorination of PVC. This liquid may be a source of interesting compounds such benzene, toluene and xylenes.

3.4 PET microwave pyrolysis: products characteristics

The poly(ethylene terephthalate) (PET) is one of the most important polyester (together with polybutylenetherephatlate, PBT) and it is used to obtain: fiber textiles, carpets, medical accessories, belts for cars, electronics and items for cars, photographic film, magnetic tapes for audio and video, packaging, bottles and so on.

The gases obtained in PET pyrolysis are mainly CO₂ (up to 22.71%) and CO (up to 13.29%) due to decarboxylation reactions involving the esters group present in the polymeric chain (Williams & Williams, 1999b).

Oxygenated compounds, like benzoic acid or other compounds soluble in aqueous NaOH, are largely found. Anyway while rising the temperature from 510°C to 610°C the concentration of oxygenated compounds decreases from 45 wt% to 29% (Yoshioka et al., 2004).

A lot of aromatics and oxygenated compounds are found in the liquid fraction, all of them coming from the therephthalic moiety present in the polymer. Their concentrations increase when rising the pyrolysis temperature.

The PET microwave pyrolysis shows very different results from the non-microwave pyrolysis. The most significant difference comes from high amount of acetaldehyde and benzene. In table 14 are reported the yields of two PET pyrolysis where chopped tires where used as microwave absorbent.

The high amount of gas is linked with the CO₂ and CO formation. The main substances present in the liquid fraction are reported in table 17; for the pyrolysis with increasing power from 1.2 to 3 kW two liquid fractions where collected when the power is changed.

Compounds	Composition %		
	1.8 to 3 (kW)	1.2 to 3 (kW)	
		Fraction 1	Fraction 2
Benzene	32.03	5.80	14.26
Toluene	9.40	4.37	9.57
1,2-dimethylbenzene	4.29	3.13	6.04
1,3-dimethylbenzene	3.70	2.31	5.25
Styrene	3.43	-	1.07
Benzaldehyde	-	1.19	-
1,2,3-trimethylbenzene	4.71	2.54	4.06
Limonene	14.51	2.31	-
1H-indene	2.44	-	-
Pentylbenzene	2.10	-	-
Benzoic Acid	5.15	1.14	-
Biphenyl	3.66	-	3.02
Total	85.42	22.79	43.27

Table 17. The main products present in the liquid from microwave pyrolysis of PET.

The acetaldehyde was identified by trapping it with (2,4-dinitrophenyl)hydrazine. The hydrazone was characterized via $^1\text{H-NMR}$.

The formation of acetaldehyde is not reported for non-microwave pyrolysis. It can be accounted as a microwave heating prerogative. The heat is provided from microwave absorbent, coal or tires, in close contact with the polymer. This heat is straight shifted from the coal to the surrounding macromolecules.

In figure 7 is reported the steps proposed for acetaldehyde formation.

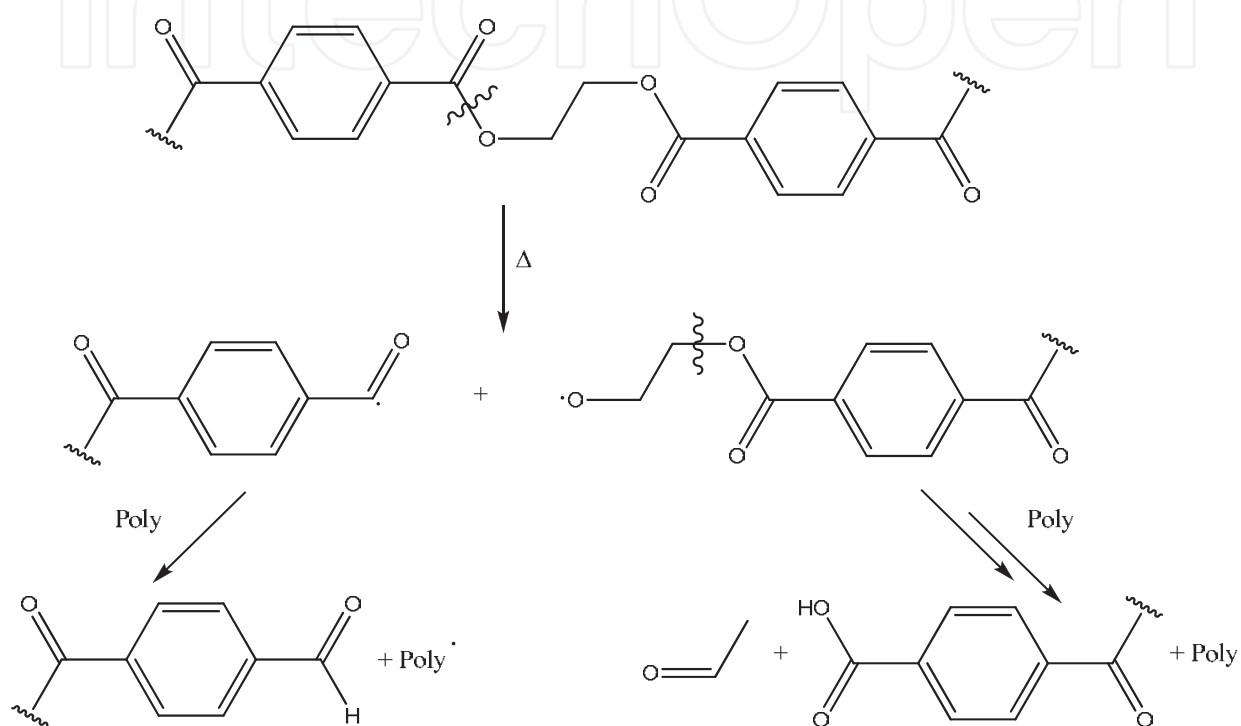


Fig. 7. Suggested reactions involved in microwave pyrolysis of PET.

3.5 PS microwave pyrolysis: products characteristics

The polystyrene (PS) is produced and sold as an amorphous polymer or as co-polymers with monomers such as acrylonitrile and butadiene.

The thermal pyrolysis of PS yields the formation of just a liquid product. A limited amount of gas is also collected (Williams & Williams, 1999b; Williams & Bagri, 2004). In the liquid product styrene is found up to 76.2 wt%. The remaining liquid fraction contains other aromatics such as: benzene, toluene, xylenes, ethylbenzene, cumene and α -methylstyrene.

The gas fraction contains: H_2 , CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , C_3H_6 and C_4H_8 (Williams & Williams, 1999b).

The PS is easy cracked also via microwave heating in the presence of a microwave absorber like with the thermal cracking. The pyrolysis leads to the complete depolymerization of PS to its monomer and other aromatics. The main products present in the liquid fraction are reported in table 18.

The yields are strongly different from a non-microwave pyrolysis (de la Puente & Sedran, 1998). The amount of styrene is lower than 50% but the amount of toluene and other aromatic compounds are higher with respect to non-microwave pyrolysis. These results

may be explained only by a different way in which the heat is transferred from the absorber to the polymer.

Compound	Composition (%)
Benzene	1.62
Toluene	8.99
1,2-dimethyl-benzene	8.70
Styrene	47.49
α -methyl-styrene	13.39
4-penthyl-benzene	5.06
Total	85.25

Table 18. The main compounds present in liquid fraction from microwave pyrolysis of PS.

4. Conclusion

Microwaves are a precious tool and they may be employed in pyrolysis process of plastics, such as HDPE, PP, PVC, PET and PS, or complex polymeric materials such as tires or mixed waste plastics. The use of a microwave heating source open new paths in waste disposal via pyrolysis, where the yields and products proprieties may be controlled just by the power of microwave it is employed. The problem of poor thermal conductivity of polymers is overwhelmed and a simpler apparatus may be employed like static bed reactors. Together with a simple apparatus the reaction time could be strongly reduced from hours to few minutes.

In addition no pretreatments are required for the polymeric waste with the exception of the addition of a microwave absorbent. Another of the big advantage in tires pyrolysis with regard to thermal pyrolysis, for instance, is the possibility to heat not chopped materials.

The microwave pyrolysis results as an optimal way to transform simple or complex plastic wastes or more generally plastic containing wastes in new products such as fuels, oil, important hydrocarbons such as BTX or to obtain gas pyrolysis non-contaminated with combustion gas and nitrogen present in the air employed for combustion and consequently the gases obtain show a high calorific value.

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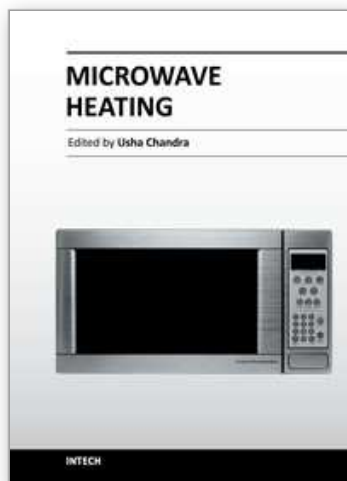
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