Potential of pyrolysis processes in the waste management sector

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ABSTRACT

The fundamentals of pyrolysis, its latest developments, the different conditions of the process and its residues are of great importance in evaluating the applicability of the pyrolysis process within the waste management sector and in waste treatment. In particular the types of residue and their further use or treatment is of extreme interest as they could become the source of secondary raw materials or be used for energy generation in waste treatments. The main area of focus of this paper is the investigation of the link between the pyrolysis conditions, the chemical and mineralogical composition of their products and the benefits of pyrolysis in the waste management sector. More specifically the paper covers the fast, intermediate and slow pyrolysis of organic waste and mixtures of inorganic and organic waste from households. The influence of catalysts during fast pyrolysis on the product yield and composition is not being considered in this review.

Contents

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1. Introduction

Each person consumes a certain amount of products, but during this process much waste is produced and discarded. The disposal of excess products and waste has been at the forefront of combating climate change. In modern societies, the average amount of waste generated by each consumer is staggering and continually increasing. It is estimated that the typical inhabitant of Western Europe produces more than 450 kg of garbage per year [1]. It must be taken into account that the whole world is committed to economic development and the continuous improvement of living conditions, thus the problem of the depletion of the limited resources of our planet and the management of waste becomes crucial. The global consumption and depletion of materials was highlighted in the Millennium Development Goals formulated in the year 2000 by the United Nations. A set of goals were formed with a heavy importance on the 7th Goal: To Ensure Environmental Sustainability [2]. Additionally, the 2008 Waste Framework Directive includes a 50% recycling target for waste from households, to be fulfilled by 2020 [3]. In 2014, in the United States, approximately 258 million tonnes of municipal solid waste (MSW) was generated. Over 89 million tonnes of the municipal waste was recycled and composted (34.6 wt%), over 33 million tonnes were combusted with energy recovery and 136 million tonnes were placed in landfills [4]. Generally, MSW covers waste from households. However, bulky waste, waste from commerce and trade, office buildings, institutions and small businesses, yard and garden waste, street sweepings, the contents of litter containers and market cleansing waste are included, too. In an expanding and developing economy, MSW is usually defined as the waste produced in a municipality, and it may be classified as either hazardous or non-hazardous. The MSW impact on the environment and quality of life is mainly related to air, water, and soil contamination. Land use, odours, and prejudice against certain types of waste treatment should also be taken into account [5].

1.1. Composition of MSW

Municipal solid waste collected mainly from households consists of plastics, paper, metals, textiles, organic waste, leather, rubber, metals, glass, ceramics, soil materials and miscellaneous other materials. Figs. 1–3 show the average composition of MSW in the USA [6], China [7] and Europe [8]. Typical household waste contains a wide range of materials that vary significantly in composition depending on the type of community and its consumers' incomes and lifestyles, and its degree of industrialisation, institutionalism and commercialism. In general, the highest waste generation is correlated with the highest income. Moreover, even the season of year or the number of persons living in a household influence the amount and composition of waste. For example, more food waste and less paper is generated during summer. Additionally, the larger the community, the more garbage is produced per capita [9].

1.2. Waste pyrolysis

Pyrolysis is the thermochemical decomposition of organic material at high temperature and in the absence of oxygen or in
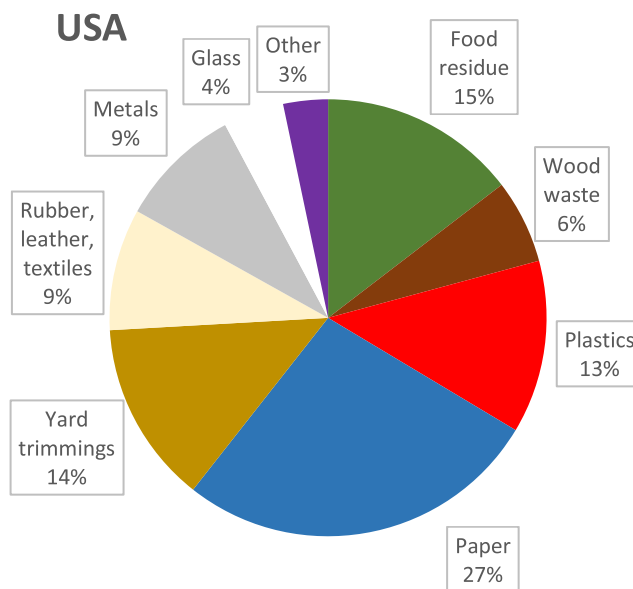

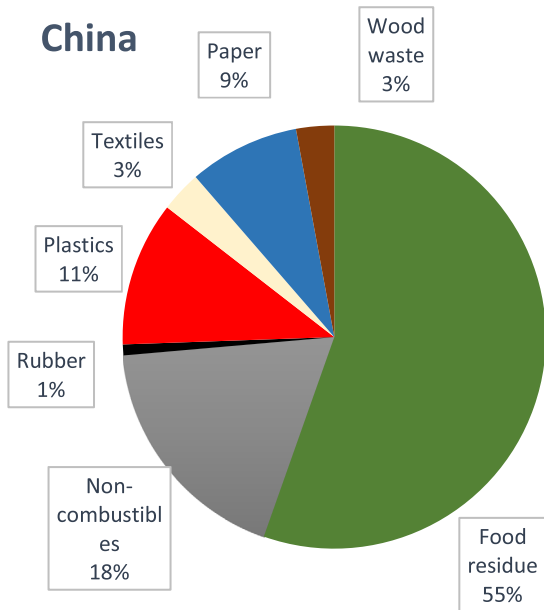**Fig. 1.** Composition of MSW in the USA [6].
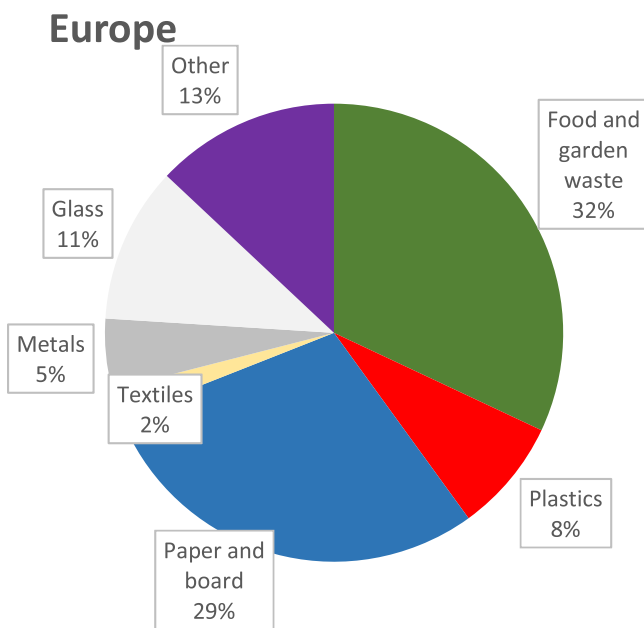
Fig. 2. Composition of MSW in China [7].

Fig. 3. Composition of MSW in Europe [8].

Fig. 4. Approximate spectra of products from different modes of thermal conversion of biomass [25].

waste can operate with a small amount of air present. Eventually this may lead to a partial gasification. In those cases, pyrolysis occurs in the inner zone of the bed. These processes are sometimes described as "quasi-pyrolysis" [15]. Other methods of thermal conversion also used in waste management are carbonisation, gasification and torrefaction. Expected yields of products from different types of biomass thermal conversion are shown in Fig. 4. Furthermore, different type of organic matter can be used to charge the reactors such as wood, organic waste (soft and hard biomass) residues from agriculture, forestry, pulping industry. Some examples are forest residues [16–19], food [20,21] and agricultural waste [22,23]. The fractions of MSW subjected to pyrolysis mainly consist of paper, cloth, plastics, food waste and yard waste. Moreover, different types of reactors have been developed, such as fixed bed, fluidized bed, tubular and pyroformed reactor or haloclean rotatory kiln. It is then easy to understand the high variability of conditions and consequently of residues obtainable. Prerequisite for the successful application of pyrolysis is the appropriate choice of input materials and the setting of optimal process conditions. For these reasons, the suitability or unsuitability of selected types of waste and their mixtures for the pyrolysis process has been verified many times by laboratory experiments with subsequent assessment of the quantity and quality of the individual products of pyrolysis [24].

2. Types of pyrolysis reactors used to utilize different domestic waste

The reactor type being used for the pyrolysis of waste has to be given great importance because of the large amount of heat to be transferred across the reactor wall to ensure material degradation [26]. Reactors described in literature used in the pyrolysis of different wastes include fixed bed reactors, batch or semi-batch reactors, rotary kilns, fluidized bed reactors, microwave assisted reactors and some innovative solutions like plasma or solar reactors. For many years, scientists have explored the mechanisms of this process in laboratories around the world, so slow, fast and intermediate pyrolysis are already well known. Several industrial waste plants successfully use or have used those processes like Waste Pyrolysis Plant "Burgau" located in Germany, which was working for 30 years (until 2015) [27]. However, there is still a big challenge to make pyrolysis economically viable, thus the next studies should focus on the implementation of the latest developments in pilots and on an industrial scale. In this section it will be

an atmosphere of inert gases. Compared to combustion, pyrolysis has a lower process temperature and lower emissions of air pollutants such as polybrominated diphenylethers (PBDEs) [10,11]. Additionally, the scale of pyrolysis plants is more flexible than incineration plants [12]. Nowadays, pyrolysis is getting attention for its flexibility to generate a combination of solid, liquid and gaseous products in different proportions just by the variation of operating parameters such as temperature or heating rate. It also provides an opportunity of transforming materials of low-energy density into bio-fuels of high-energy density, at the same time recovering high value chemicals [13,14]. One of the great advantages of this process is that many types of raw material can be used, including industrial and domestic residues. Different types of pyrolysis have been developed: fast, catalytic fast, intermediate, slow, vacuum. In practice, the processes of thermal treatment of
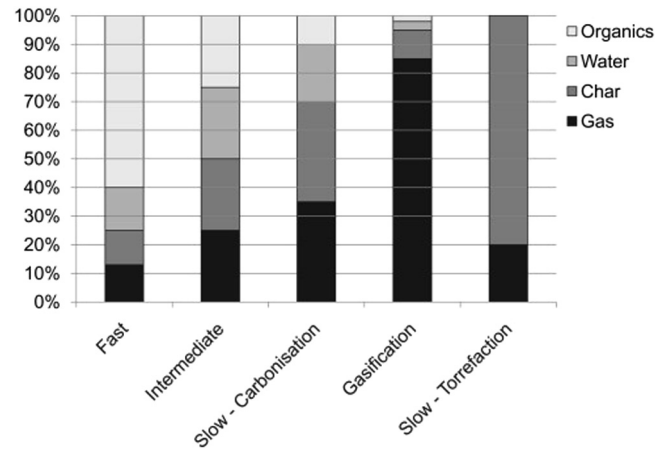
highlighted which of these solutions could be implemented as industrial solutions, instead of a use only on a laboratory scale.

Usually the pyrolysis process is conducted under atmospheric pressure. In contrast, vacuum pyrolysis is carried out under very low pressures, which can be about 5 kPa. Vacuum pyrolysis has some advantages compared to pyrolysis under atmospheric pressure because of the short residence time of organic vapour in the reactor and the low decomposition temperature, which reduces the occurrence and intensity of secondary reactions [28]. This type of reactor has been used in the pyrolysis of different types of household waste, such as wood [29], plastics [30,31], printed circuit boards [32] and tyres [33]. However, vacuum pyrolysis is difficult to achieve in practice, thus there is no information about using this process in the pyrolysis of MSW on an industrial scale.

2.1. Fixed bed reactors and batch reactors

Fixed bed reactors are the simplest solution available in laboratory-scale studies, because they are easy to design. In this type of reactor, the feedstock is placed in the reactor (often stainless steel), which is heated externally. The most popular solution is an electric furnace. Before the experiment the reactor is flushed by an inert gas (e.g. N_2, Ar) and the gas flow is maintained during the whole process in order to provide an anaerobic atmosphere. The gases and vapours obtained are discharged from the reactor during the pyrolysis, but char is usually removed after the process. The fixed bed reactor is characterized by a low heating rate. Furthermore, the feedstock does not move during the process, thus it is difficult to imagine a uniform heating of a large portion of MSW on an industrial scale. This type of reactor could be used on a larger scale provided that the technology used (e.g. heat pipes) enables better heat transfer [34]. Anyway, the fixed bed reactor is a good instrument for providing experimental information on the parameters of pyrolysis and its products.

In general, batch reactors are a closed system with no input or output of reactants or products while the reaction is being carried out resulting in high conversion. On the other hand, semi-batch reactors allow the addition of reactants and the removal of products, while the process is occurring. However, products are not uniform from batch to batch and increasing the scale is problematic [35]. The other disadvantages of this type of reactor are a long solid residence time and the difficulty of removing char.

2.2. Fluidized bed reactors

Typically, fluidised-bed reactors are used to study the behaviour of fast pyrolysis and to investigate the secondary cracking of oil at longer residence times. Fluidised-bed reactors are characterized by a high heating rate and a good blending of the feedstock. Therefore, such reactors are widely used in laboratory studies in order to describe the influence of temperature and residence time on pyrolysis behaviour and products [12]. This type of reactor seems to be a good solution for waste polymer pyrolysis. For example, polymer pyrolysis in a fluidised-bed reactor can provide remarkable advantages over the processes in other reactors in which heat is not transferred as efficiently for the cracking of polymers because polymers have a very low thermal conductivity and high viscosity [12].

On the other hand, there are important difficulties in using fluidized-bed reactors to utilize MSW. First, the raw material provided to the reactor must be tiny, so it could float in the fluid. Second, there is a big problem with separating the char from the bed material. Thus, this type of reactor is seldom used in large-scale projects. On the other hand, Ding et al. [36] proved, that it is possible to obtain high quality pyrolytic oil from MSW in a fluidized-bed reactor. However, the system was complicated and it would be problematic to scale-up. This system is shown in Fig. 5. The difficulties in sample preparation further complicate the system, and contribute towards the issues regarding viability and industrial scale up. After collection, sorting and drying, the components of MSW were crushed to small pieces. Biomass was pulverised to powder and bulked (with the maximum size being no more than 1 cm). Plastics and papers were crushed (chopped) to pieces of a length less than 5 mm. Then the components were mixed together again. The mixed raw material was dried in the oven at 80 °C for more than 48 h before each experiment, to ensure the elimination of moisture.

3. Cooling system	
3-1	Condenser 1
3-2	Condenser 2
3-3	Condenser 3
3-4	Circulating pump 2
3-5	Circulating pump 1

1. Feeding system	
1-1	Screw feeder
1-2	Electromotor & gearbox
1-3	Hopper
1-4	Water cooling tube

4. Gas heating system	
4-1	Roots blower
4-2	Diesel tank
4-3	Diesel combustor
4-4	Heating jacket 1
4-5	Heating jacket 2

2. Pyrolysis system	
2-1	Fluidized bed reactor
2-2	Cyclone separator 1
2-3	Cyclone separator 2
2-4	Char collector 2
2-5	Char collector 1
2-6	Air compartment
2-7	Gas preheater

5. Gas purification system	
5-1	Oil collector
5-2	Cyclone separator 3
5-3	Exhaust purifier
5-4	Induced draft fan

Fig. 5. Pyrolysis of MSW system based on fluidized bed reactor [36].

2.3. Spouted bed reactor

This reactor is suitable for handling particles of irregular texture, fine particles, sticky solids and those with a wide size distribution. Furthermore, the system has a great versatility with regard to gas flow, allowing operation with short gas residence times. Additionally, the excellent movement of the solids in this reactor, which leads to high heat transfer rates between phases, makes this reactor suitable for flash pyrolysis. Moreover, the conical spouted bed reactor is appropriate for continuous operation, which is especially relevant for the implementation of biomass pyrolysis at larger scale [37]. Spouted beds have also been applied successfully in studies of the pyrolysis of a number of polymers including polystyrene [38], polyethylene [39], polypropylene and polyethylene terephthalate [40]. The spouted bed reactor presents interesting conditions for the pyrolysis of waste plastics due to low bed segregation and lower attrition in comparison with the bubbling fluidized bed [39]. In this type of reactor waste plastics melt as they are being fed into the reactor and provide a uniform coating around the sand particles due to their cyclic movement. It also offers high heat transfer between phases and smaller defluidization problems with sticky solids from plastics. The solid flow pattern and the action of the spout decreases the formation of agglomerates [41]. The scheme of the conical spouted bed reactor used in pyrolysis of plastics is shown in Fig. 6. However, there is no information about the use of this reactor with mixed MSW, because they need very small pieces of feedstock to provide the advantages mentioned above.

2.4. Rotary kiln reactor

Rotary kiln reactors have been used in the slow pyrolysis of MSW in plants located in Germany and Japan among others. They usually carry out the process in temperatures around 500 °C with a residence time of about 1 h. This is the only type of reactor, which has been successfully implemented as a practical industrial solution at various scales so far [12,43,44]. However, even they may need some pre-treatment of MSW before pyrolysis. Waste should
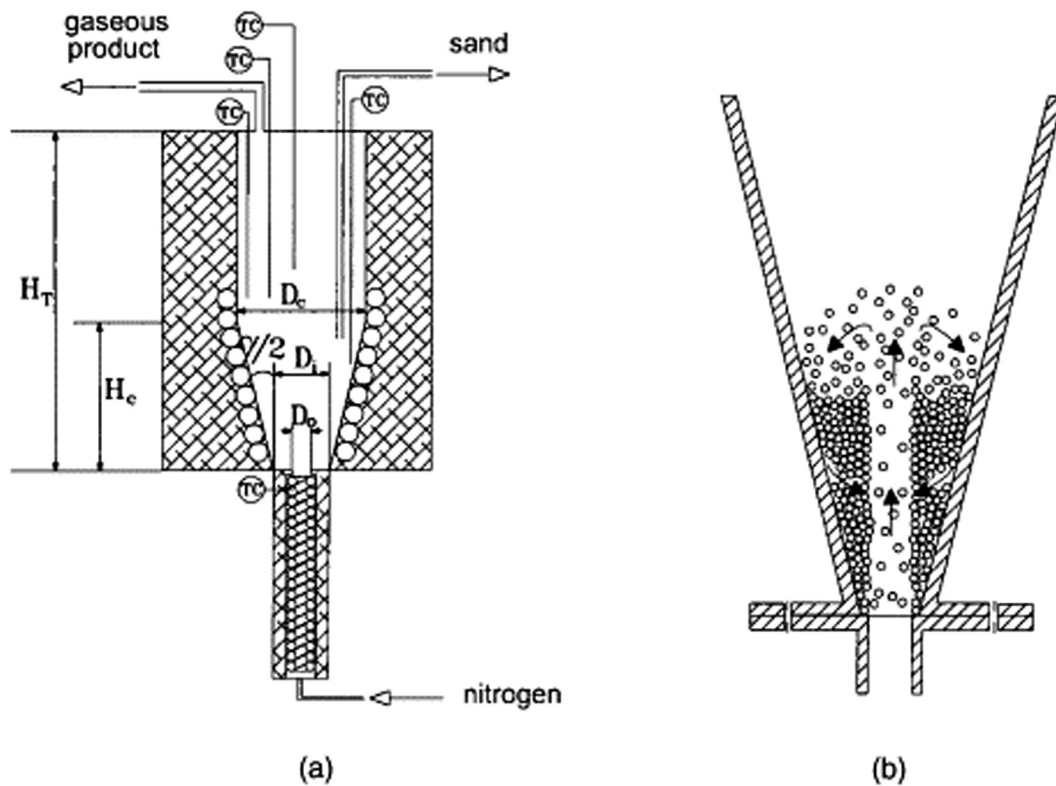
Fig. 6. Scheme and design parameters of conical spouted bed reactor used in pyrolysis of waste plastics [42].
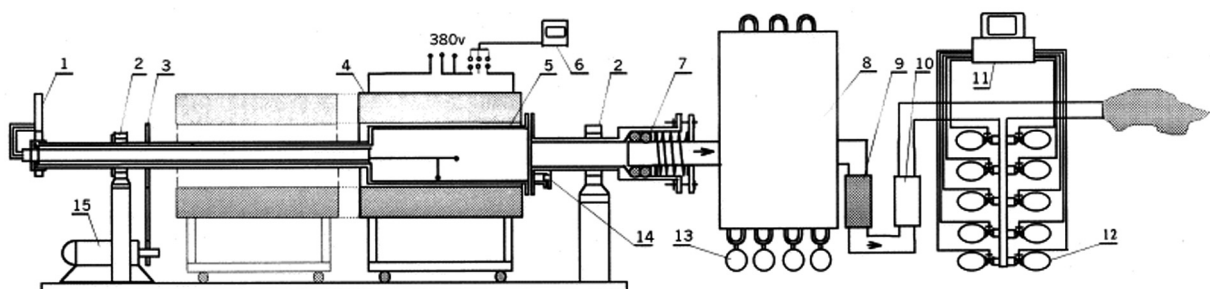
Fig. 7. Pyrolysis system based on rotary kiln reactor: (1) thermometer; (2) bearing; (3) gear transmission; (4) electrical furnace; (5) rotary kiln; (6) temperature controller; (7) seal; (8) tube type condenser; (9) filter; (10) total flow meter; (11) computer; (12) gas sampling device; (13) tar reservoir; (14) feed and discharge opening; and (15) adjustable speed electrical machinery [47].

Table 1
Comparison of microwave and thermal heating [52].

Microwave dielectric heating	Conventional thermal heating
Conversion of energy	Transfer of energy
In-core volumetric and uniform heating: the whole material heated simultaneously, energetic coupling at molecular level	Superficial heating: via convection/conduction
Rapid and efficient	Slow, inefficient, limited by material thermal conductivity
Selective: rapid intense heating for polar substances and ineffective for non polar substances	Non-selective
Dependent on material's properties	Less dependent on material's properties
Hot spots: an effect due to inhomogeneities of microwave field or dielectric properties within a material	No 'hot spots'
Precise and controlled heating: the energy input starts and stops immediately when the power is turned on or off	Less controllable

be sorted in order to remove unwanted materials and then shredded [12]. On the other hand, the preparation of waste as feedstock for the pyrolysis process is quite simple. Conventional recycling plants have to use a wide list of expensive and complicated devices, which can separate different type of polymers.

It is important, that solid wastes of various shapes, sizes and heating values can be fed into a rotary kiln either in batches or continuously; this feature allows an extensive use of this type of reactor. Rotary kilns offer better heat transfer to the feedstock than fixed beds and at the same time they are less complicated in operation than fluidized beds. The residence time of the feedstock in the reactor is a very important parameter in the pyrolysis process because it determines the energy received by the charge at a given heating rate. In rotary kilns, residence time is usually a function of

the mean volumetric flow and the rotational speed of the kiln and this was studied by Fantozzi et al. [45]. Furthermore, a rotary kiln pyrolyser has many advantages over other types of reactors. For example, the slow rotation of an inclined kiln enables a good mixing of wastes, thus it is possible to obtain more uniform pyrolytic products. Also, the flexible adjustment of residence time can make the pyrolysis reaction easy to perform at optimum conditions [46]. Fig. 7. shows the lab-scale pyrolysis system based on a rotary-kiln reactor.

2.5. Microwave assisted reactors

Microwaves lie between infrared and radio frequencies in the electromagnetic spectrum. The wave lengths of microwaves are between 1 mm and 1 m with corresponding frequencies between 300 GHz and 300 MHz, respectively. The two most widely used microwave frequencies are 915 MHz and 2.45 GHz. Microwave energy is derived from electrical energy and most of the domestic microwave ovens use the frequency of 2.45 GHz [48]. Microwave pyrolysis used in waste to energy processes was studied by Lam and Chase [49]. They accurately characterized this process, but they concluded that the growth of industrial microwave heating applications is hampered by an apparent lack of the understanding of microwave systems and the technical information for designing commercial equipment for this type of pyrolysis.

The combination of microwaves and pyrolysis has attracted much attention due to the nature and many advantages of microwave heating. The most important advantages provided by microwaves are uniform and rapid internal heating of large biomass particles, immediate response for rapid start-up and shut down, high energy efficiency, no need for agitation and controllability [50]. This solution was proposed to provide pyrolysis of paper [51], biomass [48] and plastics [26]. The comparison of conventional and microwave-based heating was summarized by Yin [52] and it is shown in Table 1. However, as observed in other

Fig. 8. Schematic of the solar pyrolysis experimental setup [55].

Soft wood　　　**Hard wood**

Fig. 9. Chemical composition of wood, wt% [61].

studies, the system faces similar issues to the fluidized-bed reactor - the feedstock particles must be very small and also the organic vapours should b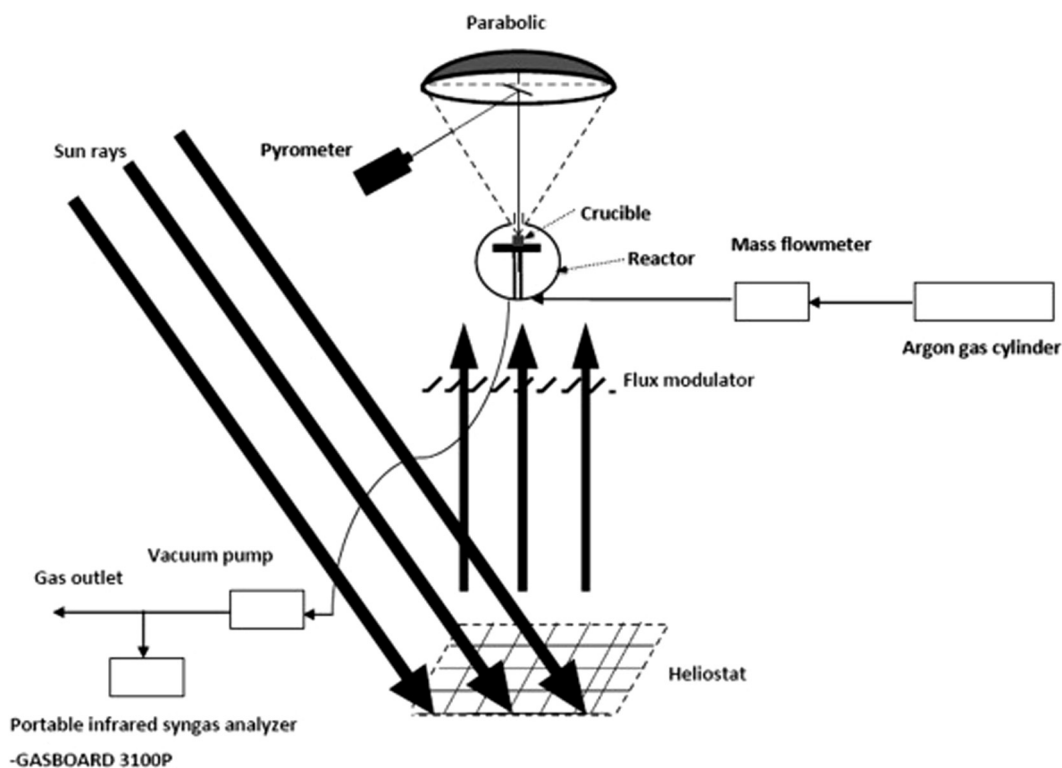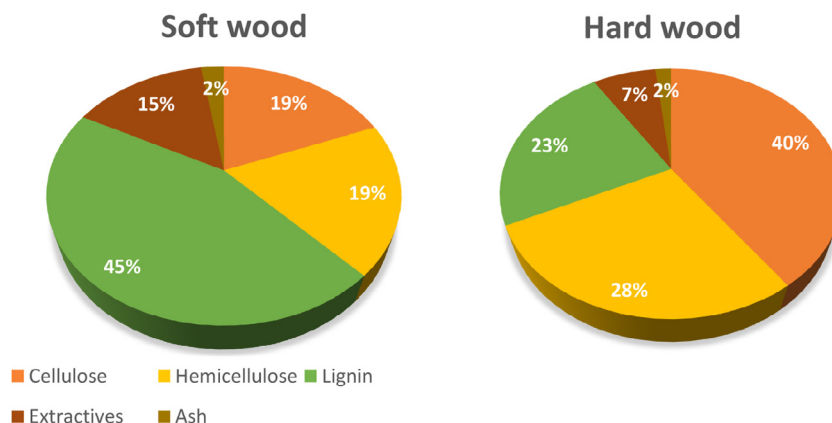e removed from the reactor very quickly in order to prevent secondary cracking reactions. Additionally, high operating costs connected with high electrical power consumption must be taken into account.

2.6. Plasma reactors

Plasma is an ionized gas considered by many to be the fourth state of matter, next to solid, liquid and gas. It can be considered as a gaseous mixture of negatively charged electrons and positively charged ions, which is created by heating a gas intensively or by subjecting a gas to a strong electromagnetic field. We can distinguish two main groups of plasmas, i.e. the high temperature or fusion plasmas and the low temperature plasmas or gas discharges. Thermal plasma generation can be achieved using a direct current or an alternating current electrical discharge or using radio frequency induction or a microwave discharge. Even a 2.45 GHz magnetron available from a commercial microwave oven can be used to produce plasma.

When carbonaceous particles derived from waste are injected into a plasma, they are heated very rapidly by the plasma, then the volatile matter is released and cracked giving rise to hydrogen and light hydrocarbons such as methane and acetylene [53]. Plasma pyrolysis is becoming of increasing interest due to its manageability, it enables fast heating, and can work effectively at relatively low power consumption [51]. Huang and Tang [53] reviewed thermal plasma pyrolysis technologies in the treatment of organic waste. Thermal plasma pyrolysis of organic waste produces only two streams: a combustible gas and a solid residue, both of which are useful and easy-to-handle products. Gas yields vary between 50 and 98 wt%. This combustible gas is composed of H_2, CO, C_2H_2, CH_4, and C_2H_4 and has a heating value in the range of 4–9 MJ/Nm^3. Thus it can be used directly as a fuel in various energy applications such as direct firing in boilers, gas turbines or gas engines. Guddeti et al. [54] reported that the solid residue from polypropylene pyrolysis contained almost 100% carbon. They observed some novel carbon structures, indicating the potential of several high value applications of this solid carbon such as production of high surface area catalysts, carbon adsorbent or electronic applications such as super capacitors.

2.7. Solar reactors

A very interesting solution for heating the pyrolysis reactor was proposed by Zeng et al. [55]. They investigated the pyrolysis of beech wood in a laboratory-scale solar reactor. The pyrolysis

experiments were carried out in a transparent Pyrex balloon reactor under an argon flow. The wood pellet was placed in a graphite crucible insulated with black foam and located at the focus of a 1.5 kW vertical-axis solar furnace. The schematic of the experimental setup is shown in Fig. 8. This construction allows the system to reach temperatures between 600 °C and 2000 °C without any additional heating sources. The aim of this study was to check the effect of temperature and heating rate on char composition and structure. The highest char yield was about 14%, which was obtained at 600 °C with a heating rate of 50 °C/s and the lowest char yield was about 6.5% when the temperature and heating rate were 2000 °C and 450 °C/s.Fig. 9

Although this is a laboratory-scale study, it deserves more attention. The possibility of using renewable energy resources to provide energy to endothermic reactions makes pyrolysis more environmentally friendly. In addition, the energy efficiency increases. This should be the direction of the latest design solutions.

3. Types of waste treated by pyrolysis and products obtained

3.1. Wood and garden waste

Each kind of biomass potentially can be used as an energy source replacing conventional fossil fuels. Municipal Solid Waste may contain significant amounts of garden waste, which are generated during maintenance of private gardens and public parks. It consists of an organic fraction (e.g. grass clippings, hedge cuttings, material from pruning, leaves, and wood) and an inorganic fraction (e.g. soil and stones) [56]. Used furniture, waste construction wood, chopsticks and toothpicks also appear in the category of household rubbish. The biomass residues can be processed in order to recover their organic content in a useful form [57]. It is noteworthy, that biomass is neutral in terms of CO_2 impacts, it emits as much CO_2 when burned as it had previously absorbed from the atmosphere, the net effect is zero [58]. In general, wood biomass is composed of three main components (hemicellulose, cellulose and lignin), with some extractives [59], and it can be divided into two basic groups: soft and hard wood. A simple chemical composition of them is shown in Fig. 8. and During the pyrolysis process the hemicellulose breaks down first at temperatures of about 200–250 °C, then cellulose decomposes in the temperature range of 240–350 °C and finally lignin is pyrolysed at temperatures of about 280–500 °C. In general, the pyrolysis of wood requires a temperature of at least 300–375 °C [59,60].

In 2015, Dalla Vecchia Torri et al. [62] published the characterisation of bio-oils derived from hard and soft wood using fast and intermediate pyrolysis. In particular their study focussed on

Eucalyptus sp. (hardwood formed by syringil-guaiacyl lignin) and the use of the most appropriate pyrolysis system for fast pyrolysis (a bubbling fluidized bed reactor), also using an alternative and more robust system and pyrolysis process (fixed bed reactor and intermediate pyrolysis). The residues were then characterized using time of flight gas chromatography and gas chromatography with quadrupole mass spectrometry. The influence of final temperature (400, 550 and 700 °C) and mass (5, 7 and 9 g) were investigated, while nitrogen flow (1 mL/min) and heating rate (100 °C/min) were kept constant in a procedure similar to the one used by Faccini et al. [17]. Raw bio-oil obtained from intermediate pyrolysis with *Eucalyptus sp.* chips had a yield of 49 ± 1.3%, while *Picea abies* residues provided 50 ± 5.7% oil. Bio-oils from intermediate pyrolysis were mainly composed of phenol, followed by ketones in both biomasses, while bio-oils from the fast pyrolysis of *Eucalyptus* residues showed a slight change in composition, with ketones as the major class, followed by phenols. Furthermore, a great number of phenolic compounds in intermediate pyrolysis bio-oils was noticed, especially methoxy derivatives of lignin breakdown, and these are related to slower heating rates, which allow the increase of secondary reactions and, consequently, the production of oxygenated compounds of lower molecular weight. In 2016, Widiyannita et al. [63] also investigated the pyrolysis of hard wood (ulin wood) at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C. As expected, the temperature significantly influenced the characteristics of pyrolysis products. The optimum temperature to produce a liquid product was 400 °C, and the highest amount of char was obtained at a temperature of 300 °C. The highest temperature pyrolysis produced char with the lowest pore size. The gas yield was the lowest pyrolysis product and it consisted mainly of CO, CO_2 and CH_4.

Kim et al. [64] checked the influence of reaction conditions on bio-oil production from the pyrolysis of construction waste wood. They used waste wood collected at a landfill site. It was a mixture of plywood, particle board, scantlings and natural wood. Material was pulverized and dried before pyrolysis. Decomposition of waste wood began at 200 °C and mass reduction took place until the temperature was about 400 °C. For both reactors used (batch reactor and fluidized bed reactor) the gas yield increased with increasing temperature (from 400 °C to 550 °C), whereas the char yield decreased with increasing temperature. The maximum oil yield was obtained at 500 °C: 54.2% and 59.9% for the batch and fluidized bed, respectively. Higher temperatures are preferable for generating gas. The gas fraction was composed mainly of CO, CO_2 and light hydrocarbons (C_1-C_4). A huge amount of carbon oxides (approximately 90%) is produced by decarbonylation of carbonyl groups and decarboxylation of carboxylic acid groups. The CO_2 fraction decreased with increasing temperature but the fractions of CO and C_1-C_4 species increased with increasing temperature. The fluidized bed reactor produced larger quantities of CO and hydrocarbons. The moisture content in bio-oil was 20–30%, which is typical for oils obtained from biomass. The moisture reduces the viscosity thus improving the fluidity and atomisation characteristics, but on the other hand decreases the heating value and can cause phase separation in the bio-oil obtained. In the applications of a fluidized bed reactor the moisture content was lower than in the case of a batch reactor. The oils consisted of the following six categories: acids, oxygenates, aromatics, phenolics, N-compounds and hydrocarbons. Oxygenates and acids reduce the heating value and stability of the oil. In the batch reactor they consisted of almost 60% of the oil, slightly less in a fluidized bed reactor, and the amount of them decreased with increasing temperature. Phenolics – which improve the oil quality - represented approximately 30% of the oils in a batch reactor and around 40% in a fluidized bed reactor and the yield increased with temperature. The authors concluded, that a

fluidized bed reactor is favourable for the production of bio-oil from wood waste. Furthermore, those reactors can be particularly useful for the production of bio-oils from the waste of the wood industry, which produces huge amounts of sawdust.

Construction wood is comparatively rare in MSW, but furniture can be found more often in waste from households. Compared with raw wood, furniture wood contains oils, adhesives, paints and varnishes used in fabrication. One of the most popular additives is formaldehyde-based resins. Thus the composition of products - especially gases - from the pyrolysis of waste furniture should be measured, to ensure there are no threats to the environment and to people. In 2010 Heo et al. [65] investigated the fast pyrolysis of waste furniture sawdust. Before the experiment the sawdust was dried at 110 °C for 24 h. The pyrolysis was carried out in a fluidized bed reactor at temperatures ranging from 400 to 550 °C. The gas composition at 450 °C was 28.0% CO, 62.3% CO_2, and 9.7% light hydrocarbons (C_1–C_4). When the temperature was increased, the char yield decreased from about 35.8% at 400 °C to 21.3% at 550 °C, while more pyrolysis vapours were released. The oil yield was a maximum of 58.1% at 450 °C and then it decreased at higher temperatures. It was noticed, that the water content in the liquid phase was high (40–60 wt%) and it might be caused by the various organic additives in waste furniture. The major components of oils were acids, oxygenates, phenolics and PAHs (polycyclic aromatic hydrocarbons). As shown in Fig. 10., the amounts of acids rapidly increased with increasing temperatures up to 500 °C. On the other hand, the oil became rapidly less oxygenated at temperatures above 500 °C because of the secondary decomposition of the pyrolysis vapours. The amounts of phenolics were high at 400 and 550 °C as there was a gradual decrease in the amount of most of the phenolic compounds, while certain compounds (phenol, 2 and 3-methyl-phenol, and 1,2-benzedediol) rapidly increased with increasing temperature.

Moreno and Font [66] studied the kinetics of waste furniture pyrolysis and the evolved gases for tests carried out at 500 °C and 850 °C in a tubular reactor. In the volatile gases evolved, the differences between furniture wood waste and solid wood are in the occurrence and concentration of nitrogen compounds. In the pyrolysis of furniture wood waste NH_3 (ammonia) was found, in the pyrolysis of raw solid wood the amount of NH_3 was insignificant. Other nitrogen compounds such as acetonitrile, 2-propenenitrile,
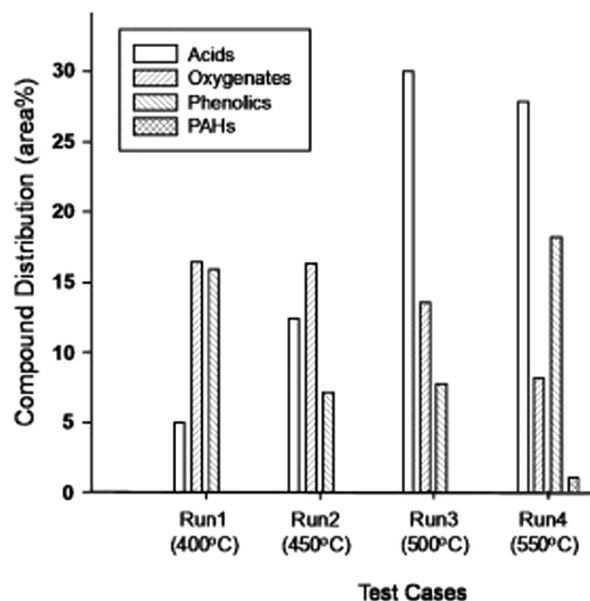
Fig. 10. Changes in composition of oil with increasing temperature in a fluidized bed reactor, in the fast pyrolysis of waste furniture sawdust [65].

Table 2
Products from the pyrolysis of wood biomass.

Type of wood	Pyrolysis condition			Pyrolysis products				References
	Reactor	Tempera-ture, °C	Heating rate, °C/min	Gas Yield, wt%	Oil/tar Yield, wt%	Details	Char Yield, wt%	
Poplar (hard wood)	Fixed bed	400	50	~26.2	~41.8	Anhydrosugars, furans, aldehydes, ketones, acids, phenols, and hydrocarbons; pH: 3.1–3.9; heating value: 11.85–14.39 MJ/kg	~32	[74]
		500		~30	~43		~27	
		600		~31.7	~41.6		~26.7	
Pine (soft wood)	Fixed bed	300	10	~10	~25	At low temperatures: wide variety of light molecular carbohydrates and their derivatives, such as saccharide, furan, carboxylic acid, ester, ketone and aldehyde (no D-glucose); at higher temperatures: many guaiacols and phenols (without PAHs)	~65	[75]
		400		~18	~53		~29	
		500		~16	~60		~24	
		600		~19	~60		~21	
		700		~20	~59		~21	
Soft wood bark	Vacuum	500		27.4	45.0 [a]	Separated into bottom and upper layer; composition: carboxylic acids, polyaromatic compounds such as naphthalenes, phenanthrenes and anthracenes, aliphatic hydrocarbons (C_{21}–C_{27}), sterols, methyl esters, phenols, benzenediols, furans, cyclopentens, alcohols and sugars; pH: 2.34–3.03; heating value: 24.3–42.4 MJ/kg	27.6	[61]
Hard wood bark			12	19.9	55.9 [a]		26.2	
Eucalyptus (hard wood)	Semi-batch	400	20	~20.5	~45	Phenol derivatives, heterocyclic derivatives, aromatic carboxylic acid derivatives; pH:1.8–2.9; heating value: 16.093 MJ/kg; flash point: 68 °C	~34.5	[76]
		500		~23.5	~47.5		~29	
		600		30.35	43.7		25.95	
Spruce (soft wood)	Horizontal tube reactor	up to 752 °C		28.9[b]	39.7[b]	Two liquid phases: an aqueous phase containing a wide variety of organo-oxygen compounds of low molecular weight and an oil phase containing insoluble organics of high molecular weight; the highest yield in 527 °C; sulphur content: 0.01 wt%	32.4[b]	[60]
Bamboo [c]	Fluidized bed	400	100	~19	~27	Very hydrophilic and thermo-active; with temperature increasing, percentage of moisture increased, while heating value of oil decreased; heating value: 21.41–28.15 MJ/kg	~26	[77]
		500		~20	~31		~20	
		600		~24	~27		~18	
		700		~33	~18		~17	

[a] oils + aqueous phase.
[b] average composition.
[c] moisture was measured separately.

Table 3
Yields from pyrolysis of different paper waste products.

Type of pyrolysis	Reactor	Tempe-rature, °C	Heating rate, °C/min	Type of waste	Product yields, wt%			Ref.
					Gas	Oil	Char	
Vacuum pyrolysis, pressure: 5 mmHg	Tubular furnace	300	10	Waste paper	12.66	42.18	45.16	[96]
		330			13.56	42.97	43.57	
		360			13.88	44.04	41.08	
		390			15.32	45.57	39.11	
		420			16.17	46.86	36.97	
		450			17.74	47.03	35.23	
Slow, reaction time: 1 h	Semi-batch	400	10		~23	~41	36	[103]
		500			~23	~45	~32	
		600			~24	48	~28	
		700			~31	~42	~27	
		800			~39	~36	~25	
		900			~44	33	23	
Slow, reaction time: 15 min	Fixed bed	800	10	Paper biomass	~53	~15	~32	[104]
Slow	Semi-batch	325	20	Paper cups	26.67	30.33	43	[14]
		350			21.27	39.23	39.5	
		375			16.87	47.13	36	
		400			13.87	52.53	33.6	
		425			26.87	42.33	30.8	
Preheated lab-scale facility	Batch reactor	400	–	Printing paper	~32	~25	~43	[98]
		500			~38	~21	~41	
		600			~41	~19	~40	
		400		Cardboard	~31	~34	~35	
		500			~40	~31	~29	
		600			~50	~22	~28	
Slow; reaction time 2 h	Packed-bed	400	10	Cardboard	~31	~39	~30	[105]
		500			~32.5	~39.5	~28	
		600			~32	~42	~26	
Fast pyrolysis	Rotating Microwave Reactor	Below 200	–	Office paper	15	42	43	[50]
Intermediate; reaction time: 150 s	Flow screw	650		Tetrapak® cartons	61	16	24	[102]
		850			76	5	19	
Slow; reaction time: 1 h	Semi-batch	400	5	Tetrapak® cartons	23.9	39.4[a]	36.7[b]	[106]
		500			23.3	51.2[a]	25.5[b]	
		600			23.9	50.7[a]	25.4[b]	

[a] char + aluminium.
[b] tar + wax,

pyrrole and pyridine, 2-methyl appear in the furniture wood waste, too. The nitrogen content can be due to the nitrogenated organic resins, such as formaldehyde-based resins. The concentration of PAHs was also measured. Significant amounts of naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene and benzo[a]anthracene were found at 850 °C. From this study, there is a need to control the emission of toxic gases from pyrolysis, especially when real waste is treated. This case shows the difference between the pyrolysis of raw solid wood (practically not found in garbage) and real wood waste. The yields of gas, oil and char from the pyrolysis of wood biomass are summarized in Table 2.

There is a lack of information about the pyrolysis of mixed garden waste, because this is mainly converted into compost, which seems be a reasonable solution to the problem of disposal. However, this process needs both a long time period and controlled conditions to result in a good quality fertilizer. If the available area is limited and the amounts of garden and food waste generated are significant, there is a need to propose a faster method to treat this type of garbage. In this case pyrolysis could be considered. Hedman et al. [67] warn against the uncontrolled burning of garden and domestic waste, because the emissions of dibenzodioxins, dibenzofurans and polychlorinated biphenyls are alarming. Some studies investigated the pyrolysis of leaves [68,69], branches [70,71], bark [61] and grass [72,73], but usually only certain species. Despite this it can be assumed that garden waste will behave during pyrolysis alike other types of biomass.

3.2. Food waste

In some areas food residue accounts for more than a half of the total waste generation. It is estimated that as much as 50% of the food produced is wasted before and after reaching the consumer, amounting to over 1.3 billion tonnes per year of food produced globally for human consumption [78]. Food waste contains lipids, carbohydrates, amino acids, phosphates, vitamins and other substances containing carbon, thus it can be a valuable source of fuels [79]. The food waste can be divided into several groups as follows: organic crop residues, catering waste and derivatives (including used cooking oils), animal by-products and mixed domestic food waste [78]. The pyrolysis of selected food wastes, such as fruit peels [80–82], potatoes peels [83], nuts shells [84–86] or bones and meat [87,88] has been investigated and reported in literature. However, many of works focused on bio-chars. Girotto et al. [89] described the problem of food waste utilization to produce useful products such as bio-oils. Pyrolysis was mentioned as a method with potential in treatment of food waste, but the effectiveness of the process is strongly dependent of waste composition. Pyrolysis of mixture of food waste have been considered in limited applications so far, because of the high composition variability of this waste.

Liu at el. [90] investigated the treatment of food waste by pyrolysis with microwave heating. Food waste was collected from a residential area in China. Fruits, plastic and shells were removed from the raw food waste, thus the remaining three main components

were white rice, vegetable leaves, and meat/ bones, with proportions of 32.69%, 44.23% and 23.08%, respectively. The measurement of the temperature profiles of food waste under different microwave powers was one of the main aims of this work. The composition of the products obtained has not been considered. When the microwave power was increased from 300 to 600 W, the yield of solid residue decreased sequentially, the gas yield increased continuously, and the bio-oil yield first increased, and then decreased. The optimal level of power for pyrolysis was 400 W. At the same time Zhang at al. [91] studied the fast pyrolysis of food waste. The conduct of the study was very similar to the investigation mentioned above. For the fast pyrolysis of food waste at 600 °C, there were various oxygenates in the pyrolysis vapour product (e.g., acetic acid; furfural; 2-cyclopenten-1-one, 2-hydroxy-; 2-cyclopenten-1-one, 2-hydroxy-3-methyl-; cyclopropyl carbinol; 1 ,4:3,6-dianhydro-πd-glucopyranose; benzofuran, 2,3- dihydro-), and there were almost no hydrocarbons and aromatics. Moreover, the oxygen content in the pyrolysis vapour product was very high - 32.26%.

Apart from the main components of pyrolysis products it is worth considering the presence of other potentially unsafe compounds. In fact, the transformation of materials during pyrolysis can produce many pollutants, such as sulphurous compounds, heavy metals, nitrogen compounds, etc. The concentration of these components is also heavily dependent on the composition of the raw material in the process. Debono and Villot [92] tried to find the reaction pathway of nitrogen compounds during the pyrolysis of various organic wastes. They examined food waste and sewage sludge from cruise ships and also common softwood from gymnosperm trees (each alone and as a mixture). A homogenous portion of 5 g of waste was placed in the reactor, which was heated at 20 °C/min to 500 °C, while purged by argon as a carrier gas. When heated, wastes were transformed into char, tars and gas. The nitrogen distribution in condensable products (char and tars) was high so that the nitrogen in the wastes is presumably stable. Researchers observed the presence of 18 nitrogen compounds in the pyrolysis gas·NH$_3$, HCN (hydrogen cyanide) and three types of compounds were identified: nitriles, heterocyclic compounds and amides. In the tars were identified 72 nitrogen compounds, which can be divided into six families: nitriles, heterocyclic compounds with one nitrogen atom, heterocyclic compounds with two nitrogen atoms, amides, amines and oximes. In organic wastes, like waste food, the main sources of nitrogen are the proteins. Hence they can be considered as the main sources of nitrogen products. Therefore, the pathway proposed in this study was based on the degradation of proteins.

In 2016 studies on the pyrolysis of food waste were carried out in Ostrava, Czech Republic. Grycová et al. [79] conducted studies on the pyrolysis of samples of waste cereal and peanut crisps at a final temperature of 800 °C. They obtained 62% and 46% of oils with a heating value 12 MJ/kg and 25 MJ/kg from peanut crisps and cereal, respectively. However, they recommended its further use for energy recovery after the separation of water, because of the noticeable water content. The gas yield was about 15–25 wt% and the gaseous components were analysed. The variation of the gas compositions as a function of temperature was clear: there was an increase in temperature accelerated hydrogen evolution. On the other hand, the concentrations of measured hydrocarbons and carbon monoxide decreased with the increasing temperature as described by Kalinci et al. [93]. The sorption capacity of chars was investigated, too. The surface area of tested pyrolysis chars was very small (below 10 m^2/g) [79]. Thus, in order to use them further, their surface area could be increased by activation and/or some chemical treatments. What is commendable, this analysis looked at all of the pyrolysis products, though to a limited extent.

3.3. Paper

Households, offices and commercial establishments are the three main sectors for paper consumption. White paper is used for academic purposes, newsprint paper is used in newspapers and corrugated cardboard is widely used in packaging. In addition, various types of paper are used for different purposes, for instance, glossy paper is used for magazines. Furthermore, paper use is widely classified into three categories, namely, industrial use (for filtering, packaging, electrical use, and wrapping), cultural use (for printing, writing, newspaper, and currency), and food packaging (for candy wrappers, food wrappers, tea bags, coffee cups and filters) [94]. This enormous consumption of paper makes it the major component of the combustible fraction of solid waste, accounting for about one third of typical municipal solid wastes. It is an appropriate combustible material and has low contents of nitrogen and sulphur. It may have sufficient feedstock for waste-to-energy utilization [51]. In 2015, 71.5% of all paper consumed in Europe was recycled, corresponding to 1.2 million tonnes more than the 70% target in 2010. In Europe, paper fibres are reused 3.5 times on average, and the world average is 2.4. Theoretically paper can be reused six to seven times, but usually it is impossible in practice [95]. Table 3. below summarises the product allocation from the pyrolysis of different type of waste paper.

3.3.1. Waste paper

Li et al. [96] investigated waste paper pyrolysis in tubular furnace pyrolysis equipment. The process was conducted at different pyrolysis temperatures and heating rates to check the product distribution, yields of pyrolysis products, and oil composition. They did not consider the composition of other pyrolysis products. Waste paper used in that experiment was collected from the waste material market. Before pyrolysis the waste paper was dried at 90 °C for 12 h to reduce the moisture content. The maximum bio-oil yield of 49.13% was achieved at a temperature of around 420 °C with a heating rate of 30 °C/min. The yield of gas increased with increasing pyrolysis temperature. The highest yield of gas of 18.23% and the lowest yield of char of 33.43% were obtained with a heating rate of 30 °C/min at a pyrolysis temperature of 450 °C. At a higher temperature, the secondary decompositions of the char and secondary cracking of vapours take place and enrich the contents of the gas product. The results of spectroscopic and chromatographic analysis showed that oil consists of many different chemical classes and there were four main different compounds in it: anhydrosugars, carboxyl compounds, carbonyl compounds and aromatic compounds. The oil consisted of two phases, one aqueous containing water, but also including appreciable quantities of acetic acid and other oxygenated compounds, and one non-aqueous containing tar, and levoglucosan. In contrast, the main components of oil obtained from the pyrolysis of paper pulp at 800 °C in descending order were naphthalene, styrene, benzene 1-ethynyl-4-methyl- and phenol [97].

Zhou et al. [98] studied the behaviour of printing paper and cardboard during pyrolysis at 400 °C, 500 °C and 600 °C. The aim of this study was to simulate real fixed bed gasifier conditions. For both type of waste, syngas yields increased, whereas char and tar yields decreased with increasing temperature from 400 °C to 600 °C. The temperature for maximum tar yield from printing paper was around 400 °C. Cardboard pyrolysis produced a higher tar yield and a lower char yield than printing paper. The gas produced consisted of CO_2, CO, H$_2$, CH$_4$ and other light hydrocarbons (C$_2$-C$_4$) and their concentration was dependent on the process temperature. The major oil components were phenolics, benzenes, naphthalenes, benzofurans and cyclopentens. Aliphatic compounds occupied a quite small fraction of the oil. This extensive study could be very useful in predicting the behaviour of paper

biomass during pyrolysis. However, it would have been good to have added the heating value of the pyrolysis products and some additional properties, which would have made it easier to evaluate their potential applications.

3.3.2. Waste paper cups

Paper cups are designed for single use and then must be disposed or recycled. Paper cups are not usually recycled; in general the disposal either leads to landfill or they are burnt in a mixture of general waste. Recycling paper cups could be potentially difficult because of their composition as a combination of paper and paraffin. A basic cup is typically made of 95 wt% of paper (cellulose wood pulp) and 5 wt% of polyethylene for coating, to improve its water resistivity and resistance to heat [14]. Paper cups may consume more non-renewable resources than cups made of polystyrene foam. This is because the wood for the paper cups has to be transported by road or rail to the manufacturing plant. The petrochemicals needed to make polystyrene cups is taken to the plant through a pipeline. Moreover, only about half the wood chips are turned into pulp paper cups. Bark and some wood waste is burned to supply energy for the process, which finally requires about 12 times as much steam, 36 times as much electricity and twice as much cooling water as the process used to make a polystyrene cup [99]. This is alarming information.

Several researchers investigated various aspects of the pyrolysis of waste paper cups [14,99,100]. For example, Jankovic [99] investigated the pyrolysis of paper cups at different heating rates up to the final temperature of 700 °C using thermo-analytical techniques aimed at obtaining a detailed mechanistic scheme of the process under non-isothermal conditions. He identified the active pyrolysis zone in a temperature range of 250–400 °C with three decomposition stages and one sub-stage. The activation energy was considered as a constant value 135.8 kJ/mol. Singh et al. [100] also made thermogravimetric analysis of waste paper cup pyrolysis. They found, that the weight loss started at 300–400 °C and finished around 500 °C. Air and nitrogen were compared as the flow medium, and the pyrolysis temperature was higher in the case of the nitrogen atmosphere. At the same time, Biswal et al. [14] studied the pyrolysis of paper cup waste in a semi batch reactor at a temperature range from 325 °C to 425 °C. The reaction time was reduced with increase in temperature (from 24 to 8 min). The maximum liquid yield was 52% at a temperature of 400 °C. The amount of gas decreased with rising temperature up to 400 °C and then increased. The highest yield of gas (26.87 %) was gained at 425 °C. The groups of compounds present in the pyrolytic oil were aldehydes, ketones, carboxylic acids, esters, alkenes, and alkanes. It was found that the pyrolytic oil contained many compounds having carbon chain length in the range of C_6–C_{18}. The physical properties of pyrolytic oil obtained were similar to other pyrolytic oils and poor quality fuels. The gross calorific value of the pyrolytic oil was 23 MJ/kg and its water content was 9.1%. It is interesting that the pour point was minus 12 °C, which may lead to freezing problems in colder regions with sub-zero climates.

3.3.3. Tetrapak® cartons

The multi-layer polycoated paperboards, often called 'tetrapaks' or 'tetra briks', are widely used as aseptic packages for beverages like milk, juice or wine. This packaging system allows products once considered perishable to be distributed and stored without refrigeration for periods of up to six months or even more. The components in tetra pack are generally kraft paper (about 70%), low-density polyethylene (approximately 25%) and aluminium foil (remainder – about 5%) [101]. The conscientious consumer, who wants to segregate waste, will have a serious problem with classifying those containers, so most of them will enter mixed waste and finally be sent to landfill. There is an urgent need to find a proper treatment method for them. Pyrolysis seems to meet the requirements, because it is a suitable treatment method both for paper and plastics. Additionally, the aluminium can be removed relatively easily from solid residue.

Haydary [102] studied the pyrolysis of aseptic packages aimed at maximum gas production and minimum tar fraction. The total amount of gas produced and also the content of H_2 and CO in gas increased with increasing temperature, while the content of hydrocarbons in gas and the total amount of liquid yield decreased. The maximum gas yield was 76% at 850 °C. The liquid fraction consisted of organic oils and water. The water and organic phases were not separated and studied in detail. Solid residue yields varied between 20 % and 25%. The proportion of carbon in the solid product decreased from 68% at 650 °C to 52% at 850 °C with the temperature increasing. However, the content of ash in the solid product increased from 21% to 26%. Aluminium residue was easily separated from the solid product. At temperatures below 750 °C, the Al was obtained without any visible structural or chemical changes, but colour and structure of the Al foil changed at higher temperatures. The remaining part of the solid product was formed of low sulphur and nitrogen solid fuel with an ash content of around 22% and heating value of 15 MJ/kg. This study shows that pyrolysis allows the effective treatment of even the most difficult waste of complex composition without damage to the environment. However, the accurate analysis of oils should be carried out in order to characterize the process entirely.

3.4. Rubber

Rubber compounds may appear in domestic waste streams, although this component is small and typically does not exceed a few percent. The biggest source of natural and synthetic rubber in waste is scrap tyres. In 2013, the used tyres in European Union countries were estimated at 3.6 million tonnes [107]. In the U.S. about 4 million tonnes was generated in 2015 [108]. Apart from tyres, other sources of rubber can be cable insulation, shoe soles and gloves, etc.

3.4.1. Tyres

Since the pyrolysis of waste tyres has been widely considered previously [109–113], it will be just briefly reviewed. In general, when whole used tyres are processed, four output streams are produced: gas, liquid (oil), solid (char) and steel. The composition of each fraction strongly depends on the pyrolysis conditions used and on the tyre composition. Temperatures of about 500 °C are considered to be optimal for the pyrolysis of tyres. The pyrolysis solid residue is mesoporous material with an average heating value of 30 MJ/kg, composed of reinforcing carbon black used in tyre production and other inorganic compounds formed during the pyrolytic process [33]. The char yield varies between about 35 and 55 wt %. The liquid-phase of pyrolysis products is usually named pyrolysis oil. Its main compounds are xylenes, trimethylbenzenes, dimethylstyrenes, dimethylindenes and limonenes and some heteroatom-containing compounds [114]. Oil yields vary between 38 and 56 wt% and the heating value is about 40–43 MJ/kg [115]. Gas obtained from the pyrolysis of waste tyres can range from a few per cent to more than ten percent of the products. It has a high heating value, up to about 84 MJ/Nm³ or 42 MJ/kg [110]. It can be said that gas-phase products from waste tyre pyrolysis generally are a mixture of paraffins, olefins (other hydrocarbons also appear), carbon oxides, hydrogen and small amounts of sulphur and nitrogen compounds.

The pyrolysis of waste tyres usually aims to maximize the yield of the liquid-phase product, because of the valuable chemicals obtained from it. Another way of improving the economics of the process is the acquisition of activated carbon from char. Moreover,

the high calorific value of the pyrolysis gas meets the energy requirements of the process and also allows the production of surplus electricity.

3.4.2. Hand gloves

Kaminsky et al. [116] studied the pyrolysis of natural rubber from hand gloves, which are commonly used in households. They obtained 18.2 wt% of gas, 80.6 wt% of oil and tar and 1.2 wt% of carbon black. The gas fraction consisted mainly of methane, CO_2, ethane and propene. Hydrogen, CO, H_2S and other light hydrocarbons also appeared. A representative sample of the raw pyrolysis oil was distilled and the distillate was separated in two phases. The polar phase consisted mainly of water, but the second phase consisted of a large variety of aliphatic and aromatic compounds such as isoprene, toluene and xylene. Additionally, the carbon black production at 600 °C was very low.

3.5. Textiles

Textile waste is considered as one of the fastest growing sectors in terms of household waste, because sales of new textiles and clothing continually increase and each new cloth finally will join the waste stream. The clothing and textile wastes are composed of synthetic materials such as acrylic, nylon and polyester fibres and natural materials such as wool, flax, leather, silk and cotton. Some studies concerning the pyrolysis of textiles are summarized below. However, there is lack of comprehensive analysis of this topic in the literature. Balcik-Canbolat et al. [117] investigated the pyrolysis of mixed waste textile fibres in a batch reactor. However, they analysed the composition of gas and char only to a limited extent and they completely neglected the liquid phase. Additional studies have been focused on char; examples of products obtained from pyrolysis of textiles are shown in Table 4.

Reed and Williams [120] examined five samples of natural fibres: hemp, flax, jute, coir and abaca, for their potential to produce activated carbon from pyrolytic char by physical activation. All of them consist mainly of cellulose (about 60%) and hemicellulose (about 12 wt% to 20 wt%) and smaller amounts of lignin, except coir, which contains more lignin (41–45 wt%) and less cellulose (36–43 wt%). The five biomass waste types were pyrolysed in a fixed bed reactor at a heating rate of 2 °C/min to the final temperature of 450 °C under nitrogen flow. The highest product yield was the liquid, which was composed of a hydrocarbon liquid with high water content. The char yield varied between 24.6 wt% from jute and 34.4 wt% from coir. The gas yield did not exceed 30 wt%, and its composition was dominated by CO, CO_2, H_2, CH_4 and C_2H_6 with minor concentrations of other hydrocarbon gases up to C_4. This composition is typical for pyrogas obtained from biomass.

Cotton is composed mainly of natural polymeric – cellulose. Thus, this material should behave like other biomass materials during pyrolysis. Chowdhury and Sarkar [13] developed the processing of Indian textile waste composed mainly of cotton. They used a fixed bed reactor heated to the temperature range 300 °C to 900 °C. The oil yield increased with increasing temperature and reached 60 wt% at 500 °C and then decreased. The highest heating value of the oil was 20 MJ/kg. Similar results were obtained by Yang et al. [105] during their investigations on the pyrolysis of textiles. In contrast the char yield decreased continuously from 75 wt% at 300 °C to 17 wt% at 900 °C. The maximum gas yield was about 40 wt% at 800 °C. The heating value of the char increased gradually from 20 to 32 MJ/kg as the temperature increased from 300 °C to 500 °C. The char was analysed using SEM. Micrographs characterized the shape and size of the char particles and their porous surface structure [13].

Acrylic textile fabric is one of the most commonly used polymers in the textile field. With acrylic fibres, the constituent polymer chains must contain at least 85% of cyanoethane (acrylonitrile) groups. The remaining 15% consists of other groups that assist fibre processing and allow the addition of several useful properties to the fibres [121]. Nahil and Williams [118] pyrolysed acrylic textile waste in a static bed reactor at temperatures between 500 °C and 900 °C. The main objective of their study was the production of activated carbon products. The char mass decreased as the pyrolysis temperature was increased from 500 °C to 900 °C, while oil and gas yields increased. However, the proportion of fixed carbon increased and the moisture content decreased with increasing temperature, thus the chars obtained at 800 and 900 °C were used in activation processes. The properties of chars obtained from acrylic textiles are shown in Table 5. The surface areas of the pyrolysis chars were less than 2 m^2/g. Activation of the pyrolysis chars with steam produced a marked increase in the surface area and porosity. The maximum surface area was obtained from char generated at 800 °C and then steam activated at 900 °C and this was 619 m^2/g.

3.6. Plastics

The world production of plastic materials reached 269 million tonnes in 2015. China is the largest producer of plastic materials, followed by Europe and NAFTA. The total European demand for plastic in 2015 was 49 million tonnes for PP, PE, PVC, PUR, PET and PS in descending order [122]. However, in municipal waste the largest fractions are: PE, PP, PS, PET and PVC [123]. Plastics

Table 4
Product yields from waste textiles: slow pyrolysis.

Reactor type	Tempe-rature, °C	Heating rate, °C/min	Gas yield, wt%	Oil yield, wt%	Char yield, wt%	References
Batch bed	500	5	~2	~40	~58	[118]
	700		~8	~41	~51	
	900		~10	~42	~48	
Packed bed	300	10	~8	~17	~75	[13]
	400		~14	~35	~31	
	500		~12	~60	~28	
	600		~22	~49	~29	
	700		~37.5	~42.5	~20	
	800		~40	~40	~20	
Fixed bed	450	5	60.35	14.00	25.65	[119]
	500		66.32	15.41	18.27	
	550		53.35	29.74	16.91	
	600		54.26	29.49	16.25	
Packed bed	400	10	~32.5	~42.5	~25	[105]
	500		~32	~45.5	~22.5	
	600		~43	~34	~23	

Table 5
Properties of chars and activated carbons from acrylic textile waste [118]

Pyrolysis temperature, °C	Char yield, wt.% of pyrolysis products	Fixed carbon,	Moisture, wt.% of char	Activation temperature, °C	C content, wt% of activated carbon	BET surface area, m²/g	Pore volume, m³/g
900	~48	79.5	1.8	800	84.8	52	0.018
				850	84.2	204	0.088
				900	87.4	373	0.180
800	~50	75.9	3.2	800	77.8	148	0.059
				850	79.7	352	0.151
				900	87.4	619	0.302
700	~51	72.3	4.6				
600	~54	69.2	4.8				
500	~58	62.6	4.5				

are much less likely to biodegrade than other organic materials in MSW. They form a heterogeneous mixture of various components with unstable internal structure and changeable external characteristics. Moreover, the contents of plastic waste vary with the region and the season [124]. As most plastics are not biodegradable, their deposition in landfills is not a desirable solution from an environmental standpoint. There is also a lot of controversy about the incineration of these wastes, due to the release of toxic and greenhouse gases [57]. For example, only very high incineration temperatures can prevent the release of dioxins and furans from plastics, but this requires huge quantities of energy. Another disadvantage of traditional incineration is that it completely destroys all organic matter, which could be valuable for different purposes. The effective treatment of plastic waste is a challenge for the protection of the environment and natural resources. The pyrolysis of plastics has been reviewed previously by Sharuddin et al. [35]. They concluded that pyrolysis has great potential to convert plastic waste to valuable, energy-bearing liquid oil, gas and char. Therefore, it is one of the best solutions for plastic waste conversion and it is also economical in terms of operation. The flexibility that it provides in terms of desired products can be achieved by changing operating parameters accordingly. However, the authors did not focus on real plastic waste mixtures, thus the following sections will expand this topic.

3.6.1. High density polyethylene (HDPE) and low density polyethylene (LDPE)

High and low density polyethylene are the largest component of waste plastic. HDPE can be characterized as a long linear polymer chain with a high degree of crystallinity and low branching which leads to high strength properties. In contrast, LDPE has more branching that results in weaker intermolecular forces, thus lower tensile strength and hardness. However, LDPE has better ductility and it is easier to mould [35]. HDPE is resistant to many different solvents and has a wide variety of applications: bottle caps, food storage containers, plastic bags, backpacking frames, banners, folding chairs and tables, fuel tanks for vehicles, piping, storage sheds, 3-D printer filaments and many more. LDPE is widely used for manufacturing various containers, dispensing bottles, wash bottles, packaging foam etc. Plastic bags are the most popular use of LDPE.

Ahmad et al. [125] studied the quality of oil obtained from HDPE pyrolysis over a temperature range of 250 – 400 °C. They found, that at 250 °C no cracking was observed. At 350 °C the conversion of HDPE into oils was the highest and oil yield reached 80.88 wt%. However, at 400 °C the gas yield had grown to 45.29 wt%, causing a decrease in oil production. The liquid fraction obtained from HDPE was enriched in naphtha range hydrocarbons with a preponderance of both gasoline and diesel range hydrocarbons. The distribution of paraffinic, olefinic, and naphthenic hydrocarbons in oil was 59.70, 31.90, and 8.40 wt%, respectively. It is

worth noting, that the Diesel index calculated for HDPE was 31.05 (Diesel – 40), which means, that this liquid fuel had excellent combustion properties. Kumar and Singh [126] used a semi-batch reactor and temperatures between 400 and 550 °C in order to process HDPE. And finally, Mastral et al. [127] conducted the pyrolysis of the same plastic above 650 °C. They used a fluidized bed, thus the solid residue was not measured, because this would present great difficulties. It is possible to see the behaviour of HDPE during pyrolysis in wide range of temperatures. Fig. 11. shows the results obtained by researchers mentioned above. It can be concluded that temperatures between 350 °C and 550 °C are the most appropriate for the pyrolysis of HDPE if the aim is to obtain liquid. Lower temperatures result in higher char yields. On the other hand, very high temperatures also reduce liquid yields.

Marcilla et al. [128] investigated the pyrolysis of low and high density polyethylene in a batch reactor. Experiments were carried out from 30 to 550 °C at 5 °C/min. In these conditions, all plastics were converted into oil and gas without a solid residue. LDPE and HDPE pyrolysis resulted in 93.1 wt% and 84.7 wt% of oil, respectively. The liquid products consisted of n-paraffins, 1-olefins and olefins in quite different proportions. Onwudili et al. [129] studied the pyrolysis of LDPE over a temperature range from 300 to 500 °C. At a temperature of 350 °C, the polyethylene pellets melted with only very small gas formation. The conversion to oil started at temperatures above 410 °C where the major product was an oily wax and the complete conversion of LDPE was conducted at 425 °C and above. Thermal decomposition produced a high yield of liquid oil with a yield of 89.5 wt% and 10.0 wt% gas at this temperature. The oil had a low viscosity dark-brown product with small amounts of waxy components. It consisted mainly of aliphatic compounds that were dominated by high carbon number alkanes followed by alkenes. Aromatics were 12 wt% of oil obtained at 425 °C (1.60 MPa pressure) and 68 wt% at 500 °C (4.31 MPa pressure). At higher pyrolysis temperatures, the oil yield
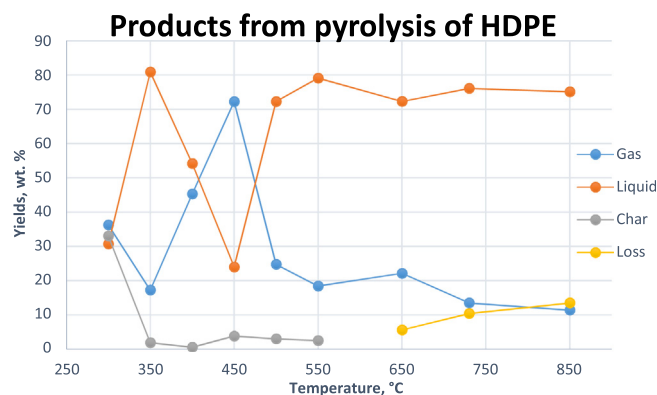
Fig. 11. Products from pyrolysis of HDPE [125–127].

decreased due to more cracking and secondary reactions leading to increasing gas formation. Park et al. [130] studied LDPE pyrolysis in order to produce light oil. They used a semi-batch reactor with agitator and the mixing rate was 100 rpm. They found that the highest oil yield was 84 wt% at 440 °C when the retention time was relatively long (132 min). This oil was characterized by low molecular weight hydrocarbon.

3.6.2. Polypropylene (PP)

Most plastic hinges, such as those on flip-top bottles, are made from polypropylene. Food containers made from it will not melt in the dishwasher, and do not melt during industrial hot filling processes. Another common application for polypropylene is with biaxially oriented polypropylene. Its sheets are used to make a wide variety of materials including clear bags. Polypropylene is also widely used in manufacturing carpets, rugs and mats to be used at home. The versatility of polypropylene is due to its good chemical resistance, mechanical properties, process ability, and its low density [131].

Abbas-Abadi et al. [131] investigated the influence of PP pyrolysis parameters on the product yield and condensed product composition. They used a semi-batch reactor and a temperature between 420 and 510 °C. The highest oil yield was 92.3 wt% at 450 °C. Higher and lower temperatures caused a decrease in oil production. Oil components were grouped into four different classes: cycloalkanes, alkanes, alkenes and aromatics. The aromatics and oleffins fractions increased but paraffin fractions decreased with increasing temperature. Abbas-Abadi et al. [131] also checked the effect of the carrier gas and stirrer rate on the product yield and oil composition. Other researchers studied the pyrolysis of PP and they obtained the highest yields of oil at high temperatures, 69.82 wt% at 300 °C and 82.12 wt% at 500 °C, obtained by Ahmad et al. [125] and FakhrHoseini and Dastanian [132], respectively. Above 500 °C the oil yield decreased with increasing temperature.

3.6.3. Polystyrene (PS)

Polystyrene is a synthetic aromatic polymer made from the monomer styrene. It can be solid or foamed, widely known as Styrofoam®. It is used in many sectors such as construction, electronics, protective packaging, toys etc. Unfortunately, polystyrene a poses serious threat to the environment, because it is non-biodegradable. Moreover, animals do not recognize polystyrene foam as an artificial material and often consume it. It is very strong and at the same time light, thus it floats on water and blows in the wind, causing a negative impact on birds and marine animals.

Achilias et al. [133] investigated the pyrolysis of raw polystyrene and plastic glasses and plastic containers also made of polystyrene. They obtained 91.8 wt% of liquid and 2.5 wt% of gas at 510 °C from model polystyrene in a bench scale fixed bed reactor. Styrene (63.9 wt% of liquid) and 2, 4-dipenyl-1-butene (14 wt%) were predominant components of the liquid with smaller amounts of toluene, α-methylstyrene, 1,2-diphenylethane and some extra compounds. Gases consisted mainly of ethane, methane, propylene and pentane-pentane. The residue was 5.7 wt%. Compared to model polystyrene, real styrene products formed a lower amount of the liquid fraction and left more residue in some cases. On the other hand, thermal cracking of polystyrene at 450 °C produced 84 wt% of liquid, 13 wt% of gas and 3 wt% of char [134]. In addition, Onwudili et al. [129] obtained a very high liquid yield, approximately 97 wt%, at 425 °C in a batch reactor. It can be concluded, that the optimal temperature for polystyrene pyrolysis should not exceed 500 °C to maximize the oil yield [35].

3.6.4. Polyethylene terephthalate (PET)

PET has become the preferred choice for plastic packaging for various food products, mainly beverages such as mineral water, soft drinks and fruit juices. This is due to its intrinsic properties that are very suitable for large-capacity, lightweight and pressure-resistant containers. PET has a wide range of applications such as prepaid cards, films, fibres and tapes, too [41]. PET has become one of the most popular plastic materials in daily life and it is often recycled. To ease the recycling process, the PET waste should be divided into different colours, but in fact it is difficult to achieve in practice. Moreover, PET bottles are bulky thus they have to be collected more frequently than other waste and therefore the transportation cost grows and more fossil fuels are consumed.

FakhrHoseini and Dastanian [132] characterized the yields of products from the pyrolysis of PET at 500 °C in a fixed bed. The heating rate varied between 6 and 14 °C/min. The solid residue yield was below 10 wt% and it decreased with increasing heating rate. The liquid product yield was the highest (almost 39 wt%) when the heating rate was the lowest. The gas yield reached 65.12 wt%. Brems et al. [135] investigated the pyrolysis of PET bottles in a fluidized bed at 420 °C to 450 °C. This temperature range was chosen after thermogravimetric analysis as the most favourable for this plastic. Vapours were condensed and the solid residue was upgraded by steam activation at pressures of up to 30 bar. The oil fraction consisted of benzoic acid and monovinyl terephthalate as major components and divinyl terephthalate, vinyl benzoate and traces of benzene occurred in lesser amounts. Additionally, char from PET pyrolysis had a good specific area – 286 m^2/g and after activation the specific area reached 1012 m^2/g, which value is comparable with commercial activated carbon.

3.6.5. Polyvinyl chloride (PVC)

PVC is one of the most important products of the chemical industry and it is a widely used plastic. In 2013 about 39.3 million tonnes of this polymer were consumed around the world [136]. This polymer is linear and strong and it is produced by the polymerization of the vinyl chloride monomer. PVC consists of 57% of chlorine and 43% of carbon [35]. The most important applications for PVC are pipes and fittings, profiles and tubes, rigid film and sheet, cables and bottles [137]. However, pyrolysis of PVC can pose a threat to the environment and humans, because highly toxic HCl (hydrogen chloride) is released. This compound is also very corrosive and can damage the pyrolysis installation. Moreover, some chlorinated hydrocarbons can also be generated during pyrolysis, and they can be precursors of toxic compounds such as polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF) and polychlorobiphenyls (PCB), when combusted [138].

Ma et al. [139] studied the pyrolysis of PVC at temperatures below 300 °C in a fixed bed reactor. The degradation of PVC started at about 200 °C and the maximum reaction rate was observed at 280 °C. At 300 °C around 50% of the PVC was volatilized. The oil yield was very low (less than 5 wt%), which is exceptional when compared with other plastics. Almost 94% of Cl from PVC was distributed into the gas phase as HCl. The liquid phase contained 5.75 wt% of the original Cl. Miranda et al. [140] carried out the vacuum pyrolysis of PVC at a temperature range of 225 °C to 520 °C in a batch reactor. The hydrogen chloride was also found to be the main product obtained from the experiment in this case with the highest yield of 58.2 wt%. The liquid oil obtained was not large and varied from 0.45 wt% to 12.79 wt% as the temperature increased. Solid residue amounts decreased with increasing temperature from 54.77 wt% at 225 °C to 8.53 wt% at 520 °C.

Yu et al. [141] reviewed the latest studies on chemical recycling methods for PVC. They found, that co-pyrolysis of PVC and biomass can reduce HCl emission. Additionally, co-pyrolysis of PVC with other plastics can lead to the stabilization of the degradation of PVC, whilst the char yield increases. It can be concluded, that PVC is not suitable for pyrolysis, because of the formation of HCl

and the occurrence of harmful chlorinated components such as chlorobenzene in the oil. Moreover, the oil yield is low. However, Yuan et al. [138] proposed a very efficient gas-liquid fluidized bed, which allowed the removal of 99.5% of Cl from released gases at a temperature of 300 °C. The HCl generated during the dechlorination of PVC was neutralized with an NaOH (sodium hydroxide) solution in two scrubbers in train. In 2011 López et al. [142] proposed several dechlorination methods devoted to reduce the chlorine content of the liquids obtained in PVC pyrolysis.

3.6.6. Polyurethane (PU)

Polyurethanes are one of the most common polymers, which are widely used in both industry and everyday life applications. Furniture, especially mattresses and the interior industry, dominates the polyurethanes market. The most common destination for end-of-life mattresses appears to be landfill, but they can be successfully treated by pyrolysis, too [143]. It is worth noticing, that polyurethanes contain N-compounds, thus the composition of the pyrogas should be examined for toxicity.

In 2015 Garrido and Font [143] studied the kinetics of the thermal degradation of flexible polyurethane foam (FPUF). Samples of material were obtained from the mattresses disposed of in a landfill in Alicante, Spain. Experiments were carried out at different heating rates to a final temperature of 900 °C. Flexible polyurethane foam appeared to degrade in a two stage process, the first around 275 °C and the other around 380 °C. The authors mentioned, that during the thermal degradation process the formation of formaldehyde, acetaldehyde, ethane, ethylene, acetylene, other hydrocarbons and other oxygenated compounds occurs. The emissions of chlorinated and aromatic compounds such as benzene, toluene and xylene have also been detected in the thermal decomposition of FPUF in an N_2 atmosphere. Herrera et al. [144] provided thermo-analytical and pyrolysis studies of nitrogen containing polymers such as rigid polyurethane (PUR). They found, that the concentration of N-containing compounds obtained during the pyrolysis was quite high but these products were not very toxic, as in the case of caprolactam and glutaronitrile. Comparing with combustion, it is possible to say again, that pyrolysis is a much safer process for the environment, because the combustion of N-containing polymers leads to the formation of toxic gases like NH_3 and HCN. These pollutants can lead to serious damage to the environment or human health.

3.6.7. Mixtures of plastics

Demirbas [145] conducted the pyrolysis of a mixture of polyolefins (PP, PE) and PS collected from landfill. The gaseous and solid yields were reported to be 35 wt% and 2.2 wt% respectively. In terms of the oil composition, the oil contained 4 ppm chlorine resulting from the PVC residue in the material. The largest part of the rest of the chlorine content was found in the solid residue. Therefore, the author concluded that the chlorine content in the feedstock should not exceed 1 wt% to ensure high quality oil was produced. The oil fraction consisted of paraffins, olefins, naphthenes and aromatics. Demirbas [145] concluded that the liquid product from plastic waste pyrolysis were a mixture of heavy naphtha (C_7–C_{10}), gasoline (C_8–C_{10}) and light gas oil (C_{10}–C_{20}) fractions; and the gaseous product typically consist of C_1–C_4 paraffinic hydrocarbons with some olefins. Co-pyrolysis of polystyrene and polyethylene carried out by Onwudili et al. [129] produced oil rich in naphthenes (cycloalkanes), n-alkanes, n-alkenes and aromatic compounds. It can be stated that the naphthenes, paraffins and olefins were direct products of polyethylene degradation, whereas the majority of the aromatics would have come from polystyrene. The calculated heating value of this liquid was 39.7 MJ/kg. Subsequently Donaj et al. [146] co-pyrolysed polyethylene and polypropylene at 650 °C and 728 °C. Gas production was 37 wt%

and 42 wt%, respectively. Solid residues did not exceed 15 wt%. In the experiments the liquid quantities were the greatest, 48 wt% and 44 wt%, respectively. However, a significant part of the liquid consisted of heavy fractions (including heavy oil, wax and carbon black). Increasing the temperature resulted in an increase in the production of lighter liquid fractions.

Mixtures of plastic waste from households were the feedstock in plasma microwave assisted pyrolysis developed by Aishwarya and Nangarthody [26]. The experimental setup comprised a modified commercial microwave oven, which had 4 magnetrons. The batch reactor was fed using a top feeder and valves permitted an inert gas to purge the plastic waste to avoid the presence of oxygen in the reactor. The oil produced from the mixture of plastics was slightly viscous and rich in aromatic compounds. However, the presence of non-aromatic compounds such as aldehydes, acids, alkynes and alkenes was also indicated. Additionally, SEM was used to describe the surface morphology of the char produced and this clearly showed the presence of pores on the surface due to the removal of volatile components.

Pyrolysis offers one more important advantage. In this process, the organic components of the material, either natural or artificial, are decomposed and the inorganic ingredients (fillers, metals, etc.) remain practically unaltered and free of organic matter and pathogens. Therefore metals could be separated and the remaining solid reused or as a last resort, the waste to be landfilled would be a minimum. Pyrolysis is especially appropriate for waste, which contains different plastics and other ingredients both organic and inorganic, for which mechanical recycling is not feasible. López et al. [147] studied the influence of waste composition on pyrolysis products. Four real samples coming from the rejects of a waste separation and classification plant located in the north of Spain were pyrolysed at 500 °C for 30 min under nitrogen. In the plant mixed wastes are passed through several complicated separation steps. After the whole process, seven reusable streams are obtained: steel, HDPE, LDPE, PET, Tetrabrik® cartons, mixed plastic and aluminium containers. These are then placed into different containers for each type of material and send to the corresponding material recyclers. About 27 wt% of the incoming raw material cannot be recovered. This rejected stream was the sample used in the pyrolysis experiments. The main components of it were as follows: packaging plastics (PE and PP together with some PS, PET and PVC), other packaging materials (metallic materials and complex packages) and inappropriate materials (e.g.: paper, clothes, wood, glass, and gardening waste). López et al. [147] prepared four samples: plastic, film rich, paper rich and glass rich with 97.03 wt%, 92.30 wt%, 43.46 wt% and 59.98 wt% of plastics, respectively. The liquid yield varied between 35.1 and 65.7 wt% and was the highest for the film rich sample. Additionally, the liquid yield from the paper rich sample contained 12.4 wt% of aqueous phase deriving from cellulosic material. Predominant components were aromatics with styrene, ethyl-benzene and toluene as the most important. The gas yield was up to 41.5 wt% in the plastic sample and char was up to 15.2 wt% in the paper rich sample. The gas phase consisted of light hydrocarbons, CO and CO_2 and small amounts of hydrogen. Paper and glass rich samples produced more carbon oxides and lower heating values. The authors concluded that the composition of the raw material significantly affected the distribution and quality of the pyrolysis products. The addition of paper led to the generation of a high proportion of an aqueous liquid phase and to large percentages of CO and CO_2. On the other hand, a high polyethylene film content resulted in the formation of high viscosity paraffinic/olefinic liquids. Finally, the presence of inorganic materials led to higher amounts of solid residues in the reactor, which is obvious.

Packaging materials are a diverse group of waste. They consist of plastics, steel and aluminium cans, tetrabrick etc. Packaging

plastics include PE and PP, with smaller amounts of PS, PET and PVC, which represent a high potential for treatment by pyrolysis. Other packaging materials are non-plastics. This group includes metals (e.g., iron and aluminium) and complex packaging materials, consisting of more than one material like Tetrapak®. Approximately 63 wt% of plastic waste comes from packing and packaging and it is about 14.5 million tonnes per year in Western Europe [148]. A highly valuable study was conducted by Adrados et al. [148]. They collected real plastic waste samples from a local material recovery facility in Bizkaia, Spain. This plant performs all separation and classification of packaging waste from Bizkaia. The composition of samples is shown in Fig. 12.

The pyrolysis of waste plastic was carried out in a non-stirred semi-batch reactor. It was heated at a rate of 20 °C/min to 500 °C, and then the final temperature was maintained for 30 min. The resulting product yields were 40.9 wt% of liquids, 25.6 wt% gases and 5.3 wt% of char. Additionally, 28.2 wt% was inorganic residue, because there were non-plastic packaging materials in the sample. Oil consisted of compounds grouped in three categories according to their number of carbons: C_5–C_9, C_{10}–C_{13} and $>C_{13}$, additionally total aromatics have been quantified. The aromatic content was very high (greater than 70%) in spite of the fact that the feedstock was composed mainly of polyolefins. The most common compounds were styrene, ethyl benzene, toluene, α-methyl styrene, xylene and naphthalene, which accounted for 33.5 %, 16.4%, 14.9%, 7.0%, 4.1% and 3.1%, respectively. The pyrogas consisted of light hydrocarbons (like methane, ethane, ethene and others with less than 6 carbon atoms per molecule), CO_2, CO and hydrogen. Its heating value was very good – circa 37 MJ/kg. An analysis of the elemental composition of the solid residue was made, too. This char had a high carbon content (29.3 wt%) and its heating value was also high and so there may potentially be opportunities for its use as a solid fuel. Other possible applications are pigments, asphalt components and activated carbons. However, the real waste of plastics contained many impurities, thus 61.4 wt% of the solid residue was ash.
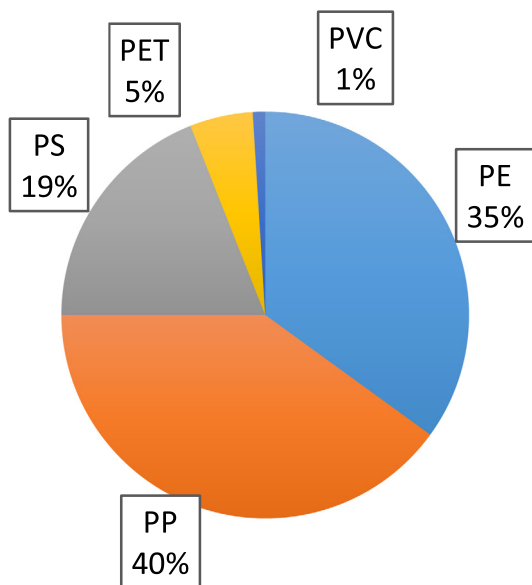
3.7. Waste electrical and electronic equipment (WEEE)

Waste electrical and electronic equipment is very diverse. Waste coming from large household appliances, fridges and freezers, CRT TV's, CRT monitors, IT and telecom, consumer electronics and small household appliances represent 27.7%, 17.7%, 13.3%, 8.3%, 8.0%, 7.8% and 7.0% of the average compositional breakdown of WEEE for the EU countries, respectively. It is estimated, that in European Union about 9 million tonnes of this waste is produced annually [152]. With rapid development of technology, higher performance requirements and greater demands on electrical and electronic equipment make their replacement ever more frequent. This situation leads to a continual increase in the number of electronic and electrical devices in our garbage.

The average composition of WEEE is shown in Fig. 13. Approximately 30 wt% of WEEE are plastics. Those plastics consist of a wide range of polymers such as acrylonitrile butadiene styrene, polypropylene, polystyrene, polycarbonate, styrene acrylonitrile, polyamide, high impact polystyrene, polyethylene terephthalate, polyethylene, polyvinyl chloride etc. [151]. Additionally, printed circuit board is a major constituent of discarded electronic scraps and it accounts for circa 30% of the total electronic scrap generated. Due to the heterogeneous mix of organic material, metal and glass fibre, printed circuit board waste is particularly very problematic to recycle [153]. Printed circuit boards are one of the main parts of electrical and electronic equipment. They are classified as FR-4 or FR-2 according to their use. The FR-4 type is composed of a multilayer of epoxy resin, fiberglass coated with a copper layer. The FR-2 type is a single layer of fiberglass or cellulose paper and phenolic coated with the copper layer. The FR-4 type is used in small devices such as mobile phones and FR-2 type is used in televisions and personal computers or other household appliances [154].

The pyrolysis of waste plastics from electric and electronic equipment and PCBs has been investigated several times [151,153,156,157]. However, the studies usually cover the thermogravimetric and kinetic analysis. Information about the composition of products and their possible uses is limited.

In 2015 Muhammad et al. [151] investigated the pyrolysis of waste plastics from WEEE. They focused on high impact polystyrene, which appears mainly in waste cathode ray tubes and acrylonitrile-butadienestyrene from waste refrigerators. Both of

Plastic waste composition

Fig. 12. The composition of plastics' real sample (wt.% with respect to just packaging plastics) [148].
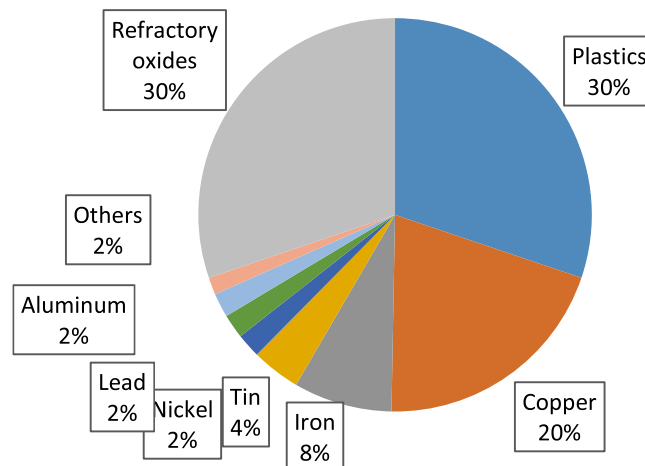
WEEE composition

Fig. 13. The composition of WEEE [155].

them have high a bromine content, because of the high content of brominated flame retardant added to those plastics. More than 80 wt% of oil was obtained in both cases. The oils ware dominated by single ring aromatic compounds with lower concentrations of polycyclic aromatic hydrocarbons (PAH). In oil from waste refrigerators about 50 wt% was styrene; toluene and ethylbenzene were slightly more than 10 wt%. However, pyrolysis of pure acrylonitrile-butadienestyrene resulted in a lower styrene concentration and higher benzene and toluene concentrations in the oil. A comparison of the pyrolysis of raw high impact polystyrene and acrylonitrile-butadienestyrene with the WEEE plastics results suggested that the WEEE plastics consisted mostly, but not exclusively, of plastics mentioned above.

Kim et al. [156] investigated the pyrolysis of a paper laminated phenolic-printed circuit board (PLP-PCB). They concluded that PLP-PCB produces brominated phenolic compounds that need to be removed from the pyrolysis oil. Long et al. [157] proposed comprehensive recycling process of waste printed circuit boards based on vacuum pyrolysis and mechanical processing. This process led to an average mass balance of 74.7 wt% solid residue, 15.0 wt% oil and 10.3 wt% gas. The residue was predominantly composed of copper, glass fibre and carbon (char and non-decomposable components). The oil was a complex mixture of organic compounds, which were mainly consist of phenol, substituted phenols, benzofuran, substituted benzofurans and bromophenols. Furthermore, the gas consisted mainly of carbon dioxide, carbon monoxide, C_1–C_4 alkanes and alkenes. Additionally, methyl bromide and hydrogen bromide appeared. The oil and gas could be used as fuels or chemical resources after proper treatment. It was suggested, that the small amounts of bromine can be easily removed from the combustion gas using existing technologies such as wet or dry scrubbing systems. The brominate compounds originating from brominated epoxy resin used in the waste printed circuit boards should be removed from oil before use, too. The solid residue was further processed to separate of copper for reuse and remove fibre glass.

3.8. Co-pyrolysis of mixtures of waste

In households the waste is often not segregated. This may be due to the lack of appropriate knowledge or for the convenience of residents. Waste materials are often not collected separately according to their criteria. Thus it is necessary to develop the co-pyrolysis of mixtures of wastes. For experiments the most desirable are mixtures, whose composition either resembles MSW composition or which are real samples of it. This approach leads to a knowledge of the real composition and yields of the products of the pyrolysis of household waste. Due to the complexity of MSW, most research has studied the pyrolysis of single components. However, the components do not act independently during pyrolysis, thus it is very important to observe their real behaviour during co-pyrolysis.

3.8.1. Biomass and plastic waste

The aim of mixing polymers with biomass wastes is to improve the liquid fraction of the products, and to evaluate the H-donor effect of polymers [158]. Biomass is hydrogen deficient chemically, where H/C_{eff} usually varies between 0 and 0.3 and it is the main reason of low petrochemical formation from biomass feedstock. On the other hand, waste plastics mainly consist of polyolefins, with a value of H/C_{eff} of 2. Therefore, carbon and hydrogen will be exchanged during co-pyrolysis of them and the quality of petrochemicals will increase [104]. What is important, household waste is largely composed of biomass, paper and plastics. In traditional waste management methods, this is a problem because there is usually a tendency to separate biomass which is then processed

in biological processes; plastics can be directed to combustion or recycling. This usually requires the use of a complex and energy-intensive waste sorting system. In the case of pyrolysis, the co-existence of plastics and organic matter in waste is a definite advantage, which lowers the outlay on waste pre-treatment and increases the efficiency of the whole process.

In 2009 Paradela et al. [57] studied the slow co-pyrolysis of pine wood and the major plastic components of Municipal Solid Wastes in proper balance. Experimental conditions highly influenced the product yields and their composition. An increase in reaction temperature from 350 °C to 450 °C led to a decrease in the liquid fraction and a corresponding increase in the gas and char products. Temperature also had a significant influence on the gas composition. At lower temperatures, the formation of CO and CO_2 was favoured, and at higher ones, the alkane formation was higher, which led to a better quality of the syngas obtained. Additionally, the increase of the reaction time between 5 and 30 min caused an increase in the alkane content of the gas fraction, at the expense of a decrease in the CO and CO_2 content. The increase in this parameter also led to an increase of the aromatic content of the liquid fraction, with a corresponding decrease in the aliphatic hydrocarbons formed.

Chattopadhyay et al. [104] used as polymer feedstock commercially available high density polyethylene (HDPE), polypropylene (PP) and polyethylene terephthalate (PET) beads. Paper used in our daily writing and domestic purposes were used as the biomass feedstock material. The paper had the following composition: cellulose 76.5 wt%, hemicelluloses 15.2 wt%, lignin 3.3 wt% and water extractives of 5 wt%. Chattopadhyay et al. [104] investigated the co-pyrolysis of plastics and paper in different proportions at 800 °C. Pure paper biomass was converted into gas, liquid and char, which were approximately 53%, 15% and 32%, respectively. On the other hand, pyrolysis of a mixture of plastics made it possible to obtain about 51.5% of gas, 21% of oil and 27.5% of char. Clear synergistic effects have been observed between biomass and plastics during co-pyrolysis, resulting in the increase in liquid products with more plastic content in the feedstock, while gaseous and solid products have followed the inverse trend. Usually there is several times more biomass than plastics in MSW. The most representative would be a sample containing three times more biomass than plastic. The pyrolysis of such a mixture gave about 55% of gaseous products, 17% of liquids and 30% of solid residue.

In 2015 Xue et al. [159] investigated the co-pyrolysis of red oak wood and high density polyethylene in a continuous fluidized bed reactor in a temperature range from 525 to 675 °C. Also Grieco and Baldi [160] checked the interaction of polyethylene mixed with biomass (paper and beech wood sawdust) during co-pyrolysis. They used pellets of waste instead of the powder usually used before, because pellets can give rise to internal transport phenomena of heat and mass closer to the actual conditions in commercial processes. They noted that the amount of char and gas increased by increasing the biomass materials and the amount of oil decreased. The same conclusion was made by Paradela et al. [57]. In general, the presence of a lignocellulosic material resulted in a strong decrease of ethylene and C_3 hydrocarbons (originating from plastic), and a significant increase in CO and CO_2 (derived from biomass). In turn, hydrogen, methane and ethane are less affected by sample composition. Bernardo et al. [149] investigated the pyrolysis of PE, PP and PS with pine biomass. Their aim was to check the physico-chemical properties of the chars obtained. Pyrolysis was carried out in a stirred batch using an initial nitrogen pressure of 0.41 MPa and a temperature of 420 °C for 15 min. The char obtained contained some liquid-phase residue and metals, mainly Mg, Ca, K and Fe. In order to improve properties these components were removed. Chattopadhyay et al. [104] analysed the influence of different catalysts on the composition of oils and

gas. However, none of those papers has analysed the composition of char and derived oils in relation only to the process temperature. Such a comprehensive analysis would be very valuable to use in industrial practice.

3.8.2. Paper sludge and municipal solid waste

Some researchers used MSW as an addition in the pyrolysis of industrial waste. This idea was developed by Fang et at. [161]. They investigated the co-pyrolysis of paper sludge and municipal solid waste. The samples for a non-isothermal co-pyrolysis experiment were heated from room temperature to 1000 °Cat heating rates of 30, 40, and 50 °C/min, with a nitrogen flow rate of 80 ml/min. The initial decomposition temperature of MSW was 267 °C while paper sludge was 306 °C, almost 40 °C higher. MSW was considered as a mixture of food waste, fruit waste, wood, paper, PVC and textiles. The pyrolysis residue masses of MSW and paper sludge were 17.45% and 53.88%, respectively. The terminated temperature for MSW (927 °C) was about 60 °C higher than that for paper sludge. All of the above indicates that paper sludge might contain more substances unsuitable for pyrolysis, such as the inorganic minerals in residual coatings, kaolin, talc, mica and other ash. Therefore, the addition of MSW into paper sludge can improve the pyrolysis characteristics.

3.8.3. Plastics, tyres and forestry biomass

Paradela et al. [162] expanded their previous study [57] and investigated the pyrolysis of mixtures of plastics, tyres and forestry biomass wastes in order to maximize liquid yields. They used 5 mm diameter particles of polyethylene, polystyrene and polypropylene, shredded pine (one of the most popular types of wood) and tyres pieces (without metal). Mixtures with these three wastes in different compositions were pyrolyzed to identify the advantage of any synergetic effects. The following range of experimental conditions of slow pyrolysis was used: temperature 350–450 °C and reaction time 5 to 30 min. The authors summarized, that the increase in plastic content in the blend increased liquid yield (from 33% to 92%) and the conversion of aromatic compounds into alkanes and alkenes, significantly decreasing the content of aromatic compounds. A decrease in CO_2 production in the pyrogas was also observed, while the release of hydrocarbons increased, thus leading to a gas with a higher heating value. Increasing the reaction temperature caused gas production with a higher content of alkanes (from 39% to 70%), although the yields of liquids decreased (82% to 74%). This expanded analysis led to the selection of the following experimental conditions as the most favourable: reaction temperature of 420 °C, reaction time of 20 min and waste mixture composition with 80% plastics, 10% pine and 10% tyres. However, this blend does not exist in reality. Sorting waste and then mixing them in appropriate proportions is not profitable in practice. Laboratory tests may indicate that if source-segregated waste is available, the pyrolysis process should be carried out with a higher proportion of artificial materials than usually is found in mixed waste streams.

Bernardo et al. [149] chose the same waste combination in order to obtain good quality char. However, the proportion was different: 30 wt% of pine wood, 30% of tyres and 40% of plastics. The conditions of pyrolysis were quite similar. Pyrolysis was carried out in a stirred batch at a temperature of 420 °C and the reaction time was 15 min. The authors obtained 60 wt% of liquid, 10 wt% of gases and 25% of char. The char was upgraded by sequential organic solvent extractions with high yields of removal of the pyrolysis liquid-phase products and removal of major metallic elements like Zinc. The upgraded char was mainly mesoporous and macroporous with significant adsorption capacity and the BET surface area was 91.4 m^2/g.

3.8.4. Orange peel, tissue paper and PVC

An interesting study was conducted by Zhou et al. [163]. Because food residue, plastics and paper compose the major part of MSW, they decided to observe the interactions between orange peel, tissue paper and PVC during pyrolysis. They checked the composition of gases obtained during co-pyrolysis. They found, that the interaction of orange peel and tissue paper was small. The interaction of orange peel and PVC was noticeable, and stopped the production of alkyls and alkenes and also weakened the peaks of HCl and C_6H_6. The interaction of tissue paper and PVC was significant; these interactions promoted pyrolysis at low temperature (below 300 °C). The residue of tissue paper and PVC increased due to interactions and the generation of CO_2, alkyls, alkenes, and carboxyls was strongly influenced. It has been reported that the char of a mixture of cellulose and PVC had fewer hydroxyl groups and more C = O and C = C bonds compared with the char of pure paper. However, an artificial mixture of waste, no matter how accurate, cannot be as valuable as a real portion of MSW. Data obtained can be carefully used as an indication for designing real processes of MSW treatment using pyrolysis.

3.8.5. MSW samples

Checking the composition and quality of products from the pyrolysis of MSW using real samples is one of the best ways of providing information for the process, thus some researchers have investigated the pyrolysis of MSW samples. In laboratory scale experiments the sample pyrolyzed is usually specially prepared, that is, dried and ground into very small particles and then thoroughly mixed to unify the composition. It is relatively easy to see what happens during the pyrolysis of a small homogeneous sample of material under laboratory conditions. Under real conditions we are dealing with a highly heterogeneous mixture of MSW (with large elements like tyres or furniture) with significant fluctuations in moisture content. Building a reactor that will provide adequate heat transfer into feedstock to ensure its decomposition with reasonable energy consumption is a difficult task. Thus there is limited information about a MSW pyrolysis plant on an industrial scale. When a suitable project is proposed, laboratory results can be used to compare the process effectiveness at small and large scale.

Luo et al. [164] checked the influence of particle size on the pyrolysis of MSW. The collected MSW samples were from a transfer station in Wuhan, China; they were dried and crushed and then separated into three different size fractions (below 5 mm, 5–10 mm and above 10 mm). Pyrolysis was carried out in a lab-scale fixed bed reactor and the bed temperature was varied from 600 to 900 °C. Particle size and temperature had integrated effects on product yield and composition: a higher temperature resulted in higher gas yield with less tar and char, and, at the same temperature, dry gas yield increased with a decrease in particle size, and
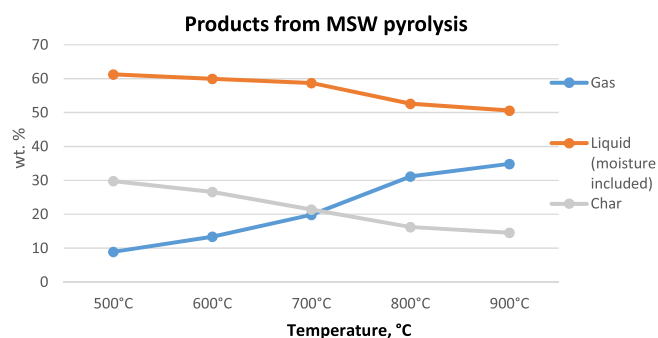
Fig. 14. Yields of products from pyrolysis of MSW sample [12].

Table 6
Yields of products from plastics pyrolysis and oil properties.

Type of reactor	Temperature, °C	Heating rate, °C/min	Type of feedstock	Gas yield, wt%	Oil yield, wt%	Details	Char yield, wt%	References
Micro reactor	300	5–10	HDPE	36.25	30.70	Composition: paraffins 59.70%, olefins 31.90%, naphthenes 8.40 %, no aromatics; flash point: 48 °C; kinematic viscosity at 40 °C: 5.08 mm^2/s; heating value: 30.6 MJ/kg	33.05	[125]
	350			17.24	80.88		1.88	
	400			45.29	54.17		0.54	
Stirred batch reactor	425	10	LDPE	10	89.5	Total conversion to liquid product, dominated by aliphatic hydrocarbons (paraffins 44 wt%, olefins 11.6 wt%) and aromatics around 9.5 wt%	~0.5	[129]
	450			25	72.4	Paraffins and olefins (C$_5$-C$_{30}$), mainly heptane to pentadecane; aromatics: 23 wt% (dominated by toluene and m/p-xylene); calculated heating value: 40.4 MJ/kg; low viscosity	1.75	
	500			47	~37.5	Dominated by aromatic compounds (65–70 wt%) mainly toluene, xylene, benzene, ethylbenzene, propyl benzene, allyl benzene and butyl benzene, naphthalene and alkyl naphthalenes; paraffins and olefins: 17.8 wt% and 3.58 wt%, respectively	15.5	
Micro reactor	300	5–10	PP	28.84	69.82	Composition: paraffins 66.55%, olefins 25.87%, naphthenes 7.58 %, no aromatics; flash point: 30 °C; kinematic viscosity at 40 °C: 4.09 mm^2/s; heating value: 35.5 MJ/kg	1.34	[125]
	350			30.00	67.74		1.56	
	400			31.07	63.23		5.7	
Stirred batch reactor		10	PS		~97.0	Major compounds: aromatics (benzene, toluene, ethylbenzene, styrene, cumene, alpha-methyl styrene, diphenylpropane and triphenylbenzene); calculated heating value: ~37 MJ/kg		[129]
	450			~0.5	~80.0		19.6	
	500			2.50	~67.0		30.4	
Fixed bed reactor	500	8	PET	57.72	34.16	No information, paper is focused on yields of products and process modelling	8.12	[132]
		10		60.23	32.13		7.64	
		12		63.03	30.33		6.61	
Batch reactor	225		PVC	44.35[a]	0.45	Kinetic study, limited information about derived oil, the highest yield of volatile HCl	54.77	[140]
	250			45.56[a]	0.5		53.49	
	260			46.16[a]	1.55		51.25	
	320			57.54[a]	3.7[b]		37.66	
	360			58.23[a]	5.0[b]		36.17	
	520			58.54[a]	32.39[b]		8.53	
Stirred batch reactor	420	5	50% plastics; 50% wood	12	54	No information; paper is focused on char	22[c]	[149]
Fixed bed reactor	800	10	HDPE, PE, PET (1:1:1)	~51.5	~21	Main components: olefins (ethylene, propylene and smaller amount of butene); aromatics (benzene, toluene, naphthalene, xylene and others); the inclination of liquid products with more plastics content in the mixture	~27.5	[104]
			50% of plastics and 50% of paper	~54	~17.5		~28.5	
Semi-batch reactor	500	20	Waste plastics	25.6	40.9	93.4 wt% aromatics; dominated by styrene, toluene and ethyl-benzene; heating value: 36.6 MJ/kg	28.2 + 5.3[d]	[148]
			Simulated waste plastics	34.0	65.2	73.9 wt% aromatics; dominated by styrene, toluene and ethyl-benzene; heating value: 43.3 MJ/kg	0.8	
Quartz tube	500	10	HDPE and waste newspaper (1:1)	~29.5	~56.5	Two phases: aqueous and oil; composition: phenols, alcohols, ketone, carbonyl, aliphatic hydrocarbons and aromatic compounds among others; water content: 0.5–1.2 wt%; pH: 4.5–4.8; density: 1.14–1.24 g/cm^3; heating value: 26.78–34.79 MJ/kg	~14	[150]
			HDPE and waste newspaper (2:1)	~23.5	~68.5		~8	
Fixed bed, two-stage batch	500	10	Plastics from waste cathode ray tubes, mainly HIPS	~9	~84	Single ring aromatic compounds with lower concentrations of 2–4 ring polycyclic aromatic hydrocarbons (PAH); mainly styrene, ethylbenzene and toluene; comparing with oil form pure HIPS and ABS: more styrene and less ethylbenzene	~7	[151]
			Plastics from waste refrigerators, mainly ABS	~8	~82		~10	

[a] mainly HCl.
[b] liquid + tar.
[c] 12% losses.
[d] inorganic + char.

char and tar yield decreased. The differences due to particle size in pyrolysis performance practically disappeared at the highest temperatures tested. Smaller particle sizes resulted in higher H_2 and CO contents from the pyrolysis of MSW and minimizing the size of raw materials is a method of improving the gas quality of MSW pyrolysis. There would be though a need to extend the processing waste line with a powerful shredder and it would be very difficult to achieve such fragmentation of mixed MSW. Furthermore, every additional device means more power consumption and extra costs.

Chen et al. [12] reviewed the pyrolysis of MSW in 2014. A mixture of kitchen waste, paper, cloth, bamboo, plastics and glass was pyrolyzed at temperatures ranging from 500 to 900 °C. The yields of products obtained are shown in the Fig. 14. Additionally, the heating value of char increased with increasing temperature from 18.3 MJ/kg at 500 °C to 30.4 MJ/kg at 900 °C. As shown, the highest yields of liquid phase and char were obtained at 500 °C. Increasing the temperature caused an increase in gas production and a decrease in char and oil.

Velghe et al. [165] compared fast and slow pyrolysis of MSW samples from a treatment plant. The average calorific value of waste was 27 MJ/kg and the samples were dried before pyrolysis. A semi-continuous lab-scale reactor was used. Slow pyrolysis was characterized by a 2 h residence time and a slow heating rate (4 °C/min) up to 550 °C. In contrast, fast pyrolysis was characterized by a short residence time (only few seconds) at a constant temperature of 450, 480, 510 and 550 °C. Slow pyrolysis produced approximately 48 wt% of liquid (30.5 ± 2.1 wt% water-rich and 17.5 ± 2.1 wt% oil) followed by about 18 wt% of solid residue and 34 wt% of gas. The best temperature for fast pyrolysis was 510 °C and at this temperature the oil yield was the highest, 67.0 ± 0.4 wt%. This liquid fraction contained the highest yield of waxy material and oil. The oil has the lowest water content and a satisfactory heat heating value, which makes it promising as fuel. The oil fraction was rich in aliphatic hydrocarbons (63.5% with 44.1% alkenes) besides 23.5% of aromatic compounds. C_8–C_{28} aliphatic hydrocarbons can be useful as chemical feedstock in several industries. On the other hand the slow pyrolysis resulted in no waxy fraction in the liquid product. The liquid product obtained separated into a water-rich fraction and an oil fraction. The oil yield was low but its composition consisted mainly of aliphatic hydrocarbons (more than 70%), which are highly desirable as a source of valuable chemicals. Apart from having a low water content the oil has a heating value comparable to that of Diesel, which makes it a good candidate for use as a fuel. Furthermore, the gas phase obtained also had excellent properties. It contained mainly hydrocarbons and had a heating value of around 20 MJ/Nm³. Ethane, ethene, propene, 2-methyl-1-propene, pentane, 2-methyl-1-pentene, and acetaldehyde were present in significant proportions and the gas can be valuable as feedstock for the chemical industry, too.

Dong et al. [166] also studied the pyrolysis and gasification of MSW, but they chose a fluidizing bed. They considered the influence of temperature and moisture content on the MSW conversion. A simulated waste sample was composed of food waste (29 wt% rice and 29 wt% cabbage), cardboard (13 wt%), plastic (17 wt% polyethylene and 3 wt% polyvinyl chloride), textile (2 wt%), timber (5 wt%), and rubber (2 wt%). The moisture content was 9.2 wt%. The temperature played an important role in MSW pyrolysis and researchers found that the syngas yield rose from 60.1 wt% or 1.0 Nm³/kg$_{MSW}$ at 550 °C to 68.8 wt% or 1.2 Nm³/kg$_{MSW}$ at 850 °C. At the same time tar and char yields decreased. The major components of the syngas obtained at 650 °C were CO, H_2, CO_2, C_2H_2, CH_4, C_2H_6 and C_2H_2 with the concentration about 9 mol.%, 5.5 mol.%, 5 mol.%, 4 mol.%, 3 mol.%, 0.5 mol.% and 0.1 mol.%, respectively. The lower heating value was approximately 6 MJ/

Nm³. Because the next step after pyrolysis was gasification the researchers did not consider the char or liquid composition. However, the syngas properties made it good gaseous fuel.

4. Pyrolysis products and their possible applications

Usually the pyrolysis of waste is aimed at energy recovery, because the products often have good properties as fuels. Moreover, energy (especially electricity) is always a desirable product, which is easy to sell. Additionally, parts of the products can be combusted in order to meet the pyrolysis energy demand. Pyrolysis also makes it possible to convert waste into an energy source for the home [34], and on a larger scale pyrolysis plants may use the pyrolysis products for other purposes, which increases the profitability of the process. The complex composition of pyrolytic oil and some properties of char could make them favourable as a raw material for some industry sectors and a few propositions are mentioned below.

4.1. Pyrolytic gas

In general, it is possible to say that the composition of the pyrolytic gas is strongly dependent on the pyrolysis temperature and feedstock. Slow pyrolysis of biomass waste such as wood, garden waste and food residue at low temperatures (below 400 °C) produces small amounts of gas, which is high in CO_2, CO and light hydrocarbons. The yields of gas at these conditions usually do not exceed 30 wt% of products. Increasing the temperature causes an increase in gas yields, because of the secondary reactions and partial char decomposition. The gas heating value from slow pyrolysis is around 10 – 15 MJ/Nm³ and varies in dependence on temperature and heating rate [167]. Fast pyrolysis of biomass produces gas with a heating value around 14 MJ/Nm³. On the other hand, higher temperatures (above 700 °C), especially when pyrolysis is combined with gasification, produces syngas, which contains more hydrogen and carbon monoxide. In this case gas is the main product of the process. The pyrolysis of plastics produces pyrolytic gas, of which the major components are hydrogen light hydrocarbons: methane, ethane, ethene, propane, propene, butane and butane. This gas has a significant calorific value, e.g. a heating value of gas from PP and PE varied between 42 and 50 MJ/kg [168]. Similar properties characterized the gas from the pyrolysis of tyres or other artificial products like textiles. In turn, co-pyrolysis of polymers and biomass leads to a higher production of CO and CO_2 especially at lower temperatures. Finally, the pyrogas from MSW consists of CO_2, CO, hydrogen, methane and other light hydrocarbons with an average heating value of around 15 MJ/Nm³, which increases with increasing temperature [169]. The most suitable demand on pyrogas is its use as a source of the energy required for the pyrolysis process itself. However, the exhaust gas has to be controlled. Pyrogas from tyres contains a relatively high concentration of H_2S, which can be oxidized to SO_2 [170]. PVC pyrolysis produces huge amounts of HCl [35]. Finally, food waste processing could be a source of dangerous nitrogen compounds [92]. Usually the precise composition of waste is not known, thus some unwanted compounds can appear in pyrogas. Therefore, emission control units and gas cleaning devices should be used and it does not matter whether the gas will be combusted or not.

4.2. Pyrolytic oil

Pyrolytic oil offers more opportunities for use than gas, but, depending on the composition of the feedstock and the process parameters, the composition of the liquid product from pyrolysis may differ radically. Pyrolytic oils originating from biomass consist

largely of the following compounds: acids, sugars, alcohols, ketones, aldehydes, phenols and their derivatives, furans and other mixed oxygenates. Phenolic compounds are often present in high concentrations (up to 50 wt%), consisting of relatively small amounts of phenol, eugenol, cresols, xylenols, and much larger quantities of alkylated (poly-) phenols [171]. They can be used for the production of heat, electricity, synthetic gas or chemicals. Temperatures between 500 and 600 °C provide the highest yields of oil, when biomass is processed with heating values of around 15–20 MJ/kg. On the other hand, pyrolytic oil from plastics has a higher heating value, about 30 – 45 MJ/kg, depending on the polymer and it contains a smaller aqueous fraction. Ahmad et al. [125] compared the oil from the pyrolysis of PP and HDPE with Gasoline and Diesel (see Table 7). Physical properties such as viscosity, the research octane number and the motor octane number, pour point, flash point or Diesel index could be a good indication of pyrolytic oil quality as a fuel [125,172]. The heating value of oils from mixed plastic waste could be estimated at 40 MJ/kg [147,148].

Detailed information about oils obtained from different plastics and their mixtures with other waste is shown in Table 6. It can be summarized, that the liquid phase is usually the predominant product of the pyrolysis of plastics. Those oils are a valuable material, which can be used in a variety of ways. Some examples are mentioned below. The oil obtained from the pyrolysis of polyethylene at 425 °C consists of more than 30 wt% of the aliphatic fractions from C_{12} to C_{18} and alpha-olefins. In detergent industries those components are highly desirable feedstocks for the manufacture of raw materials such as alkyl benzene sulphonic acid and sodium lauryl ether sulphate [129]. Donaj et al. [146] even proposed the concept of feedstock recovery from the waste polyolefin. This concept is shown on Fig. 15. The feed of the pyrolysis is the mixture of polyolefins that can be extracted from MSW. Waste plastics should be comminuted to approximately 1–5 mm pieces. The pyrolysis is conducted at 600–700 °C in a fluidized bed reactor. The yields obtained from the pyrolysis of plastic give directly 15–30% gaseous olefins from the waste, which can be used immediately in a polymerization plant. The liquid consisting of naphtha-like components has to be upgraded to olefins or other chemicals using available petrochemical technologies. Some of the lower-value hydrocarbons can also be used for providing energy for driving the pyrolysis process. Researchers concluded that refining polyolefins only via pyrolysis (with an efficiency of 25%) can cover up to 20% of the total monomer feedstock, increase the rate of waste recovery and reduce the consumption of fossil fuels.

On the other hand, the valorization of the oil from PET is less obvious, because of the acid or esterified nature of these products and PET monomers are absent. If upgrading fails, these products can be used as fuel [135]. However, even pyrolysis of real plastic waste consisting of polyethylene, polypropylene, polystyrene, polyethylene terephthalate and polyvinyl chloride allows the extraction of a valuable liquid fraction. The pyrolysis liquids have a high heating value (~37 MJ/kg) so that they can be used as an alternative to fossil fuels. This oil also contains significant amounts of styrene, toluene and ethyl-benzene; thus it can be a source of
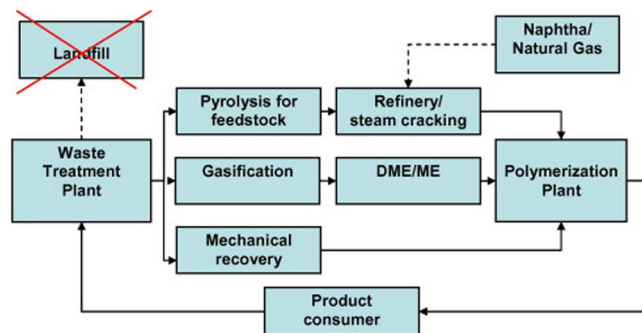
Fig. 15. The concept of waste polyolefins recovery [146].

chemicals [148]. These aromatics are highly valuable as solvents, and as precursors for a wide variety of compounds including drugs, lubricants, detergents, plastics (e.g., polystyrene, polycarbonate), and explosives. The possibility of obtaining valuable aromatic hydrocarbons from plastic waste makes pyrolysis more attractive, even though an efficient extraction of such chemicals is not easy to achieve.

Finally, co-pyrolysis of plastic and biomass, two of the most important components of MSW, produce liquid consisting of an aqueous phase and tar as shown by Brebu et al. [173]. In comparison with the thermal degradation of biomass alone, co-pyrolysis produces less aqueous phase and more oil. The char yield decreases also. Moreover, the pyrolysis tar obtained from biomass was reddish brown with an irritable odour, whereas the oil obtained from co-pyrolysis was yellow in colour with the typical odour of petroleum hydrocarbons. The tar contained a high amount of water even after separation of the aqueous phase. On the other hand, oils from co-pyrolysis consisted of hydrocarbons. The heating value of oil varied between 41 and 46 MJ/kg. Rutkowski and Kubacki [174] additionally checked the density, pour point and total acid number when polystyrene was added to the cellulose. In general, co-pyrolysis of biomass and synthetic polymers could be an environmentally friendly way for the transformation of waste into valuable products such as chemicals or fuels. Moreover, co-pyrolysis allows the simplification of expensive and complicated waste separation and classification processes and it still provides valuable products.

4.3. Pyrolytic char

Pyrolysis conditions are usually optimized in order to maximize the liquid and gas products; however, a solid fraction named as pyrolytic char is also produced. This char mainly consists of a carbon-rich matrix that contains almost all the inorganic compounds present in the raw wastes and a significant amount of condensed by-products formed during the pyrolysis process and dispersed throughout the solid porous structure [151]. The heating value of char obtained from co-pyrolysis of waste (mixture of

Table 7
Comparison of pyrolytic oil from some polymers with standard liquid fuels [125].

Properties	HDPE	PP	Gasoline	Diesel
Heating value (MJ/kg)	40.5	40.8	42.5	43.0
Viscosity at 40 °C (mm²/s)	5.08	4.09	1.17	1.9–4.1
Density at 15 °C (g/cm³)	0.89	0.86	0.780	0.870
Research octane number	85.3	87.6	81–85	–
Motor octane number	95.3	97.8	91–95	–
Pour point	−5	−9	–	6
Flash point	48	30	42	52
Diesel index	31.05	34.35	–	40

Table 8
BET surface area of biochar obtained from different type of wood.

Wood	S_{BET}, m^2/g	Pyrolysis conditions			References
		Temperature, °C	Heating rate, °C/min	Residence time	
Bamboo	277.3	550		30 min	[176]
Pine	186	474		12–15 min	[175]
Poplar	175.77	400	50	10 min	[74]
	411.06	600	30		
Spruce	196	500	12.6	30 min	[177]
Almond tree	204	600		1 h	[86]

biodegradable and non–biodegradable) is approximately 34 MJ/kg [63], which is comparable with typical coal. However, as expected some heavy metals and other hazardous elements, like S, Cl and N, may also be retained in the solid products. Therefore, it is important to fully characterize chars to assess their impact on the environment and humans. In general, this product can be combusted to provide energy for the pyrolysis process or other purposes.

Char obtained in pyrolysis is not only a good fuel, but it can also be processed into activated carbon. This possible application was investigated by Zeng et al. [55]. Char reactivity was measured in order to find a correlation between the evolution of the char surface area and pore volume and the temperature and heating rate. Experiments were performed at four heating rates of 5, 50, 150 and 450 °C/s to the final temperatures of 800, 1200 and 2000 °C; and then two other temperatures of 600 °C and 1600 °C with the heating rate of 50 °C/s were used. The chars obtained mainly consisted of carbon with mass content higher than 75%. At a temperature of 2000 °C the char was completely carbonized with almost 100% carbon content. Additionally, the BET surface area increased from 70 m^2/g to 110 m^2/g and adsorption volume increased also from 0.0028 cm^3/g to 0.047 cm^3/g when the temperature increased from 800 °C to 1200 °C with a heating rate of 50 °C/s. Southern yellow pine wood pyrolyzed at 474 °C in a pilot scale pyrolysis plant produced bio-char with 70.27% of fixed carbon and 186 m^2/g measured surface area [175]. Table 8. shows the BET surface area of biochar obtained from different types of wood reported in literature.

Theoretically, any raw material with a high carbon content could be used to produce activated carbon. In practice, coal, coconut shells, wood, peat and fruit stones are most commonly used to manufacture activated carbon [118]. However, in a laboratory scale study, an enormous range of alternative raw materials has been used to produce activated carbons. The use of waste materials to produce activated carbon is preferable because it reduces the cost of producing activated carbons. An interesting application of char from the pyrolysis of mixtures of wastes is its valorisation as an adsorbent of pollutants. Usually, the pyrolysis chars have porous structures compatible with adsorption purposes. Moreover, due to their potential adsorptive properties, the solid chars are good precursors for manufacturing activated carbons by means of physicochemical activation. In 2012 Bernardo et al. [149] checked the physico-chemical properties of chars obtained in the co-pyrolysis of wood and plastics among others. The prevalent metal in char obtained from the co-pyrolysis of plastics and biomass is magnesium (Mg). Calcium (Ca), potassium (K) and iron (Fe) are significant elements in this char, too. However, zinc (Zn), chromium (Cr), nickel (Ni), molybdenum (Mo), manganese (Mn) and aluminium (Al) also appear. Researchers used sequential solvent extraction with solvents of increasing polarity in order to remove the pyrolysis liquid-phase products from the char. This led to significant removal efficiencies, particularly for Mg, Ca and K. At the same time a significant amount of pyrolytic oil was recovered, improving the yield of liquid products. Since no activation treatment was performed the char presents relatively low surface areas.

The carbonaceous materials obtained have sufficient quality to be reused as precursors for adsorbents.

Another application of char from the pyrolysis of wood is its use as an organic fertilizer, which offers many advantages. Biochar increases the retention of nutrients and water in soil and provides habitats for symbiotic microorganisms, thus crop yields increase. Moreover, biochar can also fix carbon for many years due to the strong resistance of its aromatic carbon structure to biological decomposition [178]. Peters et al. [179] simulated a slow pyrolysis system for generating heat and biochar from lignocellulosic energy crops and its life-cycle performance was compared with that of direct biomass combustion. Coarse wood chips (50–100 mm particle size) from plantation were used, then dried to 7% water content and ground in order to get 3 mm particle sizes. After that, biomass was converted by slow pyrolysis into gas, tars and a char product. The gases and tars produced are burned on site for heat generation, satisfying the heat demand of the pyrolysis reactor and generating heat for other uses. The most desirable product - the biochar slurry - was transported from the pyrolysis plant to the field by truck and spread like manure. Researchers averred that coproducing biochar and heat by slow pyrolysis shows significant GHG abatement potential. It gives significantly higher GHG savings than direct biomass combustion, basically due to biochar effects on biomass yield and carbon sequestration in the soil.

5. Conclusion

The continual increase in the amount of waste produced by society makes clear the urgent need for developing new and better methods of disposal. Traditional waste management methods like composting, landfilling and incineration are outdated and should be replaced by modern, effective and easy-to-operate solutions, such as pyrolysis.

Pyrolysis of MSW on an industrial scale is carried out in rotary kilns, because they provided sufficient heat transfer with relatively low energy consumption. The use of modern heat transfer technologies combined with traditional fixed bed is also promising.

Pyrolysis allows the utilization of all carbon-containing materials both organic and inorganic as opposed to commonly used biological methods of waste disposal. In general, slow pyrolysis of organic waste (wood, food and garden waste, paper, natural textiles etc.) is usually carried out at temperatures about 400–500 °C and heating rates of 5–20 °C/min under nitrogen flow. Fast pyrolysis is more complicated, but it is also used. Addition of inorganic waste (plastics, artificial textiles, tyres) results in improved product quality: gas contains more light hydrocarbons and less CO_2; liquid contains a lower aqueous fraction and a greater oil fraction, and has a better heating value. The combination of organic and inorganic waste occurs in MSW, thus pyrolysis is a favourable method for waste treatment. Raising the temperature results in higher gas yields and lower char and oil yields. If polyvinyl chloride, polyurethanes, tyres or electric and electronic equipment are present in pyrolysed waste, the emissions should be closely

monitored as hydrogen chloride, hydrogen sulphide, brominated and chlorinated compounds, and variety of N-compounds are present in the products.

Pyrolysis gives ready-to-use fuels in an easy and safe way. Usually gas and/or char are used as a source of energy, because energy is the easiest product to utilize and sell. Liquid products from pyrolysis of MSW are very complex and usually contain water. However, the thermal decomposition of polymers produces oils with good qualities, which can be used both as a liquid fuel or as a source of chemicals. Additionally, after quality control and/or some improvement char can be used as activated carbon or fertilizer.

As has been reported in this paper, pyrolysis should be further developed in the waste management sector and the following activities are recommended for future work:

- improving the energy efficiency of the process and the products quality;
- eliminating any undue emissions from the pyrolysis' process;
- minimizing the pre-treatment of waste;
- developing technologies that allow for the efficient processing of mixed waste stream.

It may be beneficial also to implement next-generation technologies that are available on the lab-scale as an industrial solution; and to look for new solutions that would eliminate the problem of waste disposal on domestic level altogether.

Acknowledgement

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