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Potentials 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 their relative residues are of great importance to evaluate the applicability of the pyrolysis process within the waste management sector and waste treatments. In particular the type of residues and their further use or treatment is of extreme interest as they could become the source of secondary raw material or generate beneficial influence 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 specific the paper covers the fast, intermediate and slow pyrolysis of organic and a mixture of inorganic/organic charge from households. The catalysts influence during fast pyrolysis on products yields and composition is not being considered in the review.

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Keywords: household waste; MSW; biomass; paper; plastics; food waste; pyrolysis

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1. Introduction

Each person consumes a certain amount of produce, but during this process a large amount of 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 amount of waste generated by the average consumer is staggering and constantly increasing. It is estimated that the statistical inhabitant of Western Europe produces more than 450 kg of garbage per year [1]. Generally, municipal solid waste (MSW) covers waste from households and consists of plastics, paper, metals, textile, organic waste, leather, rubber, metals, glass, ceramic, earthen materials and miscellaneous other materials. Typical households waste contain a wide range of materials that significantly vary in composition depending on the type of community and its consumers' incomes and lifestyles, and its degree of industrialisation, institutionalism and commercialism [2]. In some areas such as China, more than half of waste produced in household are food waste [3].

Pyrolysis is the thermochemical decomposition of organic material at high temperature and in absence of oxygen or inert gases atmosphere. 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 gives possibility to transforms materials of low-energy density into bio-fuels of high-energy density and recover higher value chemicals [4,5]. Different types of pyrolysis have been developed: fast, catalytic fast, intermediate, slow, vacuum. Moreover, different types of reactors have been investigated. One of the great advantages of this process is that many types of raw material can be used, including industrial and domestic residues. The fractions of MSW subjected to pyrolysis mainly include food waste, paper, cloth, plastics, and yard waste. It is then easy to understand the high variability of conditions and consequently of residues obtainable. Prerequisite for pyrolysis successful application is the appropriate choice of input materials and setting of optimal process conditions. For these reasons, suitability or unsuitability of selected types of waste and their mixtures for the pyrolysis process was verified by laboratory experiments many times with subsequent assessment of the quantity and quality of the individual products of pyrolysis [6].

2. Types of waste treated by pyrolysis

Depending on feedstock for pyrolysis process, conditions and the type of reactor used, the yields and the composition of pyrolytic products can be significantly different. Several examples of products yields form pyrolysis process according to the process parameters are shown in Table. 1. Furthermore, analysis of composition and properties of gas, liquid and solid pyrolysis products are made below.

2.1. Food waste

It is estimated that as much as 50% of the food produced is wasted before and after reaching the consumer, accounting for over 1.3 billion tons per year of food globally produced for human consumption [7]. Food waste contains lipids, carbohydrates, amino acids, phosphates, vitamins and other substances containing carbon, thus it can be a valuable source of fuels [8]. The food waste can be divided into several groups as follows: organic crop residue, catering waste and derivatives (including used cooking oils), animal by-products and mixed domestic food waste [7]. Pyrolysis of selected food waste, like: fruit peels [9–11], potatoes peels [12], nuts shells [13–15] or bones and meet [16,17] were investigated and has been commonly noted in literature. However, many of works focused on bio-chars. Moreover, there is limited information about pyrolysis of mixed food waste from households.

Liu at el. [18] 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 obtained products has not been considered. The yield of solid residue decreased sequentially, the gas yield increased continuously, and the bio-oil yield first increased, and then decreased when the microwave power increased from 300 to 600 W. The optimal level of power for pyrolysis was 400 W. In turn, *Zhang at al.* [19] studied the fast pyrolysis of food waste. The composition of the study was very similar like 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%.

2.2. Wood biomass and garden waste

Each kind of biomass potentially can be used as an energy source replacing the conventional fossil fuels. Waste from households may contain significant amounts of garden waste, which are generated during maintenance of private gardens and public parks. It consists of organic fraction (e.g. grass clippings, hedge cuttings, prunings, leaves, and wood) and inorganic fraction (e.g. soil and stones) [20]. Used furniture, waste construction wood, chopstick and toothpick also appear in household rubbish category. The biomass residues can be processed in order to recover its organic content in a useful form [21]. In general, pyrolysis of wood prefers the temperature at least 300 – 375 °C [22,23]. In 2010 *Heo et al.* [24] investigated the fast pyrolysis of waste furniture sawdust. Before experiment the sawdust was dried at 110 °C for 24 hours. The pyrolysis was carried out in fluidized bed reactor at temperature ranged 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 was released. The oil yield maximized to 58.1% at 450 °C and then decreased at the higher temperatures. It was noticed, that water content in liquid phase was high (40 – 60 wt. %) and it might be caused by the various organic additives of waste furniture. The major components of oil were acids, oxygenates, phenolics and PAHs (polycyclic aromatic hydrocarbons). 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.

There is lack of information about pyrolysis and mixed garden waste, because they are mainly converted into compost, which seems be reasonable solution. However, this process need a long time period and controlled conditions to result in good quality fertilizer. If the available area is limited and amounts of generated garden and food waste are significant, there is a need to propose faster method to treat this type of garbage. In this case pyrolysis could be taken into account. *Hedman et al.* [25] *w*arn against uncontrolled burning of garden and domestic waste, because the emissions of dibenzodioxins, dibenzofurans and polychlorinated biphenyls are alarming. Some studies concern the pyrolysis of leaves [26,27], branches [28,29], bark [30] and grass [31,32], but usually only certain species. Despite this it can be assumed that the garden waste will behave during pyrolysis alike other types of biomass.

2.3. Paper waste

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) [33]. Enormous consumption of paper by households and offices makes it one of the major component of combustible fraction of MSW. It is an appropriate combustible material and has low contents of nitrogen and sulphur, and may have sufficient feedstock for waste-to-energy utilization [34].

Zhou et al. [35] studied the behaviour of printing paper and cardboard during pyrolysis at 400 °C, 500 °C and 600 °C. For both type of waste syngas yield increase, whereas char and tar yield decreases with increasing temperature from 400 °C to 600 °C. The temperature for maximum tar yield from printing paper was around 400 °C. Cardboard pyrolysis produces higher tar yield and lower char yield than printing paper. The produced gas consisted of CO_2, CO, H_2, CH_4 and other light hydrocarbons (C_2-C_4) and their concentration was dependent on process temperature. The oil major components were: phenolics, benzenes, naphthalenes, benzofurans and cyclopentens. Aliphatic compounds occupy a quite small fraction of the oil. This extensive study could be very useful to predict the behaviour of paper biomass during pyrolysis. However, it would be good to add the heating value of the pyrolysis products and some additional properties, thus it would be easier to evaluate their potential applications.

2.4. Plastics waste

World production of plastic materials reached 269 million tonnes in 2015. In municipal waste the largest share are: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) [36]. Plastics are more difficult to be biodegraded than any 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 [37]. 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 [21]. Effective treatment of plastic waste is a challenge to the protection of the environment and natural resources. Pyrolysis of plastics was reviewed before by *Sharuddin et al.* [38]. They concluded that pyrolysis has great potential to convert the most energy from plastic waste to valuable liquid oil, gaseous and char. Therefore, it is one of the best solutions for plastic waste conversion and also economical in terms of operation. The flexibility that it provides in terms of desired product could be achieved by changing the parameters accordingly.

Interesting study was provided by *Adrados et al.* [39]. They collect real plastic waste sample from local material recovery facility in Bizkaia, Spain. This plant performs all separation and classification of waste from Bizkaia. The sample consist of 35 wt. % of PE, 40 wt. % of PP, 19 wt. % of PS, 5 wt. % of PET and 1 wt. % of PVC. The pyrolysis of waste plastic was carried out in 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. As a result, 40.9 of liquids, 25.6 gases and 5.3 wt. % of char was obtained. Additionally, 28.2 wt. % was inorganic residue, because there was non-plastic packaging materials in the sample. Oil consists 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 (>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 33.5 %, 16.4 %, 14.9 %, 7.0%, 4.1% and 3.1%, respectively. The pyrogas consist of light hydrocarbons (like methane, ethane, ethene and other with less than 6 carbon atoms per molecule), CO_2, CO and hydrogen. Its heating value was very well – 37.2 MJ/kg. The elemental composition of solid residue was made, too. This char had very carbon content (29.3 wt. %). Its heating value was very high so it may have potential application opportunities as a solid fuel. For example, other possible applications are pigments, asphalt components and activated carbons. However, real waste of plastics contained a lot of impurities, thus 61.4 wt. % of the solid residue was ash.

2.5. Samples of MSW

In households the waste is not segregated many times. It may be due to the lack of appropriate knowledge or the convenience of residents. Waste materials are often not collected separately according to their criterion. Thus it is necessary to develop the co-pyrolysis of mixtures of wastes. The most desirable are mixtures, whose composition most resembles MSW composition or just real samples of it. This allows knowing the real composition and yields of products of pyrolysis of household waste. Due to the complex of MSW, most of research has studied the pyrolysis of single components. However, the components do not act independently during pyrolysis, thus this is very important to observe theirs real behaviour during co-pyrolysis.

Velghe et al. [40] compared fast and slow pyrolysis of MSW samples from treatment plant. The average calorific value of waste was 27 MJ/kg and the samples were dried before pyrolysis. 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 for fast pyrolysis was 510 °C and in this temperature the oil yield was the highest 67.0 ± 0.4 wt. %. This liquid fraction contains 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 obtained liquid product separated itself in a water-rich fraction and an oil fraction. The oil yield was low, however, its composition exists mainly out of aliphatic hydrocarbons (more than 70 %), which are highly desired as a valuable chemicals source. The oil has low water content. Moreover, the heating value was comparable to Diesel, which makes it also a good candidate as fuel. Furthermore, obtained gas phase also had excellent properties. It contained mainly hydrocarbons and had heating value of around 20 MJ/Nm^3. In addition, ethane, ethene, propene, 2-methyl-1-propene, pentane, 2-methyl-1-pentene, and acetaldehyde were present in significant proportions and can be valuable as feedstock for the chemical industry, too.

Table 1. Products allocation form pyrolysis of different waste

Feedstock	Reactor	Temperature (°C)	Yields (wt. %)			References
			gas	liquid	solid	
Food waste	Fixed bed	800	~29	46	~25	[8]
Soft wood	Vacuum	500	24.7	45.0	27.6	[30]
Hard wood	Vacuum	500	19.9	55.9	26.2	[30]
Paper	Batch	600	~41	~19	~40	[35]
Tires	Moving screw bed	600	11.7	48.4	39.9	[41]
Textiles	Fixed bed	450	60.35	14.00	25.26	[42]
Plastics	Semi-batch reactor	500	34.0	65.2	0.8	[39]
Biomass and plastics	Autoclave	400	~9	~65	~17	[21]
MSW	Semi-continuous lab-scale	550	34.0	48.0	18.0	[40]

3. Pyrolysis products as an energy source

Usually pyrolysis of waste is aimed to energy recovery, because the products often have good properties as a fuel. Moreover, energy (especially electricity) is always desired product, which is easy to sell. Additionally, part of products can be combusted in order to meet pyrolysis energy demand.

3.1. Pyrolytic gas

In general, it is possible to say that composition of pyrolytic gas is strongly dependent on the pyrolysis temperature and feedstock. Slow pyrolysis of biomass waste such as wood, garden waste and food residue in low temperatures (above 400 °C) produces smaller amounts of gas, which is high in CO_2, CO and light hydrocarbons. The yields of gas in this conditions usually do not exceed 30 wt. % of products. Increasing the temperature causes increasing of gas yields, because of the second reactions and partial char decomposition. Gas heating value from slow pyrolysis is around 10 – 15 MJ/Nm^3 and varies in dependence of temperature and heating rate [43]. Fast pyrolysis of biomass produces gas with heating value around 14 MJ/Nm^3. On the other hand, higher temperatures (above 700 °C) especially when pyrolysis is combined with gasification produces syngas, which contain more hydrogen and carbon monoxide. In this case gas is the main product of the process. Plastics pyrolysis produced pyrolytic gas, which major components are hydrogen light hydrocarbons: methane, ethane, ethene, propane, propene, butane and butane. This gas has significant calorific value, e.g. heating value of gas from PP and PE varied between 42 and 50 MJ/kg [44]. In turn, co-pyrolysis of polymers and biomass leads to higher production of CO and CO_2 especially in lower temperatures. Finally, the pyrogas from MSW consist of CO_2, CO, hydrogen, methane and other light hydrocarbons with average heating vale around 15 MJ/Nm^3, which increasing with increasing temperature [45]. The most suitable desire of pyrogas is use them as a source of energy necessary for the pyrolysis. Combustion of this gas could provide the reactor heating. However, the exhaust gas should be controlled. Pyrogas from tyres contains relatively high concentration of H_2S, which can be oxidized to SO_2 [46]. PVC pyrolysis produce huge amounts of HCl [38]. Finally, food waste processing could be a source of dangerous nitrogen compounds [47]. Usually the precise composition of waste is not known, thus some unwanted compounds can appear in pyrogas. Therefore, emission control units and cleaning gas devices should be used and it does not matter whether gas will be combusted or not.

3.2. Pyrolytic oil

Depending on the composition of the feedstock and the process parameters composition of liquid phase from pyrolysis may be radically different. Pyrolytic oils originated from biomass consist largely of the following compounds: acids, sugars, alcohols, ketones, aldehydes, phenols and their derivatives, furans and other mixed oxygenates. Phenolic compounds 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 [48]. They can be used in order to production of heat, electricity, synthesis gas or chemicals. The heating value of pyrolytic oil from biomass is around 15 – 20 MJ/kg. On the other hand, plastic pyrolysis oil has higher heating value about 30 – 45 MJ/kg depending on polymer and contain less aqueous fraction [39,49]. However, even pyrolysis of real plastic waste consisting of polyethylene, polypropylene, polystyrene, polyethylene terephthalate and polyvinyl chloride allows the extraction of the valuable liquid fraction. The pyrolysis liquids have high heating value (36.6 MJ/kg) so that they can be used as an alternative to fossil fuels [39]. Finally, co-pyrolysis of plastic and biomass, two the most important components of MSW, produce liquid consisting of aqueous phase and tar. It was well shown by *Brebu et al.* [50]. Comparing with thermal degradation of biomass alone, co-pyrolysis produce less aqueous phase and more oil. The char yield decreases also. Moreover, the pyrolysis tar obtained in from biomass was reddish brown in colour with irritable odour, whereas the oil obtained from co-pyrolysis was yellow with typical petroleum hydrocarbons odour. The tar contained high amount of water even after the separation of the aqueous phase. On the other hand, oils from co-pyrolysis consisted of hydrocarbons. The heating value of oil varied between 41.33 and 46.43 MJ/kg. In general, co-pyrolysis of biomass and synthetic polymers could be an environmentally friendly way for the transformation biomass and plastic waste into valuable fuels [51]. Moreover, co-pyrolysis allows simplifying expensive and complicated waste separation and classification process and still providing products.

3.3. Pyrolytic char

Pyrolysis conditions are usually optimized in order to maximize the liquid and gas products; however a solid fraction named as pyrolytic char also are produced. This char is mainly composed by 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 dispersed throughout the solid porous structure [152]. The heating value of char obtained from co-pyrolysis of waste (mixture of biodegradable and non–biodegradable) was approximately 33.6 MJ/kg [63], which is comparable with typical coal. However, as it is expected that 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 char to assess their impact on the environment and humans. In general, this product can be combusted in order to provide energy for pyrolysis process or other purposes.

4. Conclusions

The constant increase in the amount of waste produced by society makes the urgent need to develop 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. One of the methods that have the greatest potential is pyrolysis. For many years, scientists explore 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. However, there is still a big challenge to make the pyrolysis economically viable, thus next studies should focus on implementation of latest developments into pilot and industrial scale. A good raw material for the pyrolysis process is basically any material, which includes organic carbon. This is a big advantage pyrolysis compared with the conventional biological waste management methods like composting and anaerobic digestion, because it does not require the use of complex waste separation at easy bio decomposable (biomass, food scraps, wood) harder bio decomposable (paper, natural fibres) and non-decomposable, artificial (e.g. plastics, artificial textiles, tires). In centralised waste management sector slow pyrolysis in rotary kilns or tubular reactors are used. However, even rotary kilns may need pre-treatment of MSW before pyrolysis. Waste should be sorted in order to remove unwanted materials and then shredded [52]. Pyrolysis can be carried out successfully at a temperature of about

300-400 °C without fear of high pollutants concentration in flue gases. Waste incineration needs much higher temperatures and complicated flue gas cleaning systems. Therefore, waste incineration plants usually are large, engineering objects. Waste has to be transported by truck, thus the fossil fuels consumption grows. Ideal solution would be the possibility of processing waste at the household level, to minimize transportation. However, burning of waste in house is extremely harmful [53]. Pyrolysis makes it possible to convert waste into energy for the house [54], and on a larger scale pyrolysis plants also use the pyrolysis products as a sources of energy. Waste incineration has to be connected with efficient and expensive flue gas cleaning system to avoid harmful emissions. Landfilling need complicated system to collect and use biogas from anaerobic digestion of organic waste. Pyrolysis gives energy and ready-to-use fuels in a definitely easier and safer way.

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