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Review

PYROLYSIS AND COMBUSTION OF SCRAP TIRE

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Abstract

In this paper a literature review of both pyrolysis and combustion processes of scrap tires is presented. The work reports, the characteristics of materials, methods, effect of various process parameters, kinetic modelling applied to the pyrolysis and combustion of tires, characteristics of the products and emissions.

From the published works results that scrap tire rubber consists of about 60 wt.% volatile organics, 30 wt.% fixed carbon and 10 wt.% ash. Elemental analysis shows that tire rubber contains approximately 80 wt.% of C, 7 wt. of H, 0.4 wt.% of N, 1.5 wt.% of S, 3 wt.% of O and 8 wt.% of ash. Thermogravimetry analysis reveals that the pyrolysis of tire rubber at atmospheric pressure starts at a temperature around 250^{o}C and finishes at a temperature of about 550^{o}C. Generally, more than one degradation temperature region during rubber pyrolysis is recorded. In general, by pyrolysing waste tire three fractions are obtained: solid residue (around 40 wt.%), liquid fraction (around 50 wt.%) and gas fraction (around 10 wt.%). The influence of the process conditions on the amount and characteristics of individual fractions was studied by the authors only partially. The general trend is an increase in yields of liquid and gas fractions as the temperature increases.

From the works devoted to tire pyrolysis, which are focussed on the generation of liquid fuel results that derived liquids are a complex mixture of organic compounds containing a lot of aromatics. This liquid can be separated into light and higher fractions. The main components of pyrolysis gases reported by various authors are as: H_2, H_2S, CO, CO_2, CH4, C_2H_4, C_3H_6 and other light hydrocarbons. The solid residue contains carbon black, and inorganic matter.

The results of kinetic modelling of scrap tire pyrolysis and combustion show large differences in the values of kinetic parameters obtained by different authors. As main pollutants from the combustion of waste tires are reported: SO_2, NO_x, CO and PAHs.

Key words: *pyrolysis, combustion, waste tire, scrape rubber*

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1. Introduction

Only in the EU, USA and Japan around 6 million tones per year of scrap tires are produced. The huge quantity of waste tires presently produced in the world will certainly increase in the future as the associated automotive industries grow. The disposal of scrap tires becomes a serious environmental problem. The accumulation of discarded waste tires leads to environmental pollution. A large fraction of the scrap tires is simply dumped in sites where they represent hazards such as diseases and accidental fires. Rubbers are not biologically degradable, and this fact creates problems with their disposal. The impact of waste rubber on the environment can be minimized by recycling with material or energy recovery. However, during processing and moulding rubber materials are crosslinked, and therefore they cannot be simply again softened and remoulded by heating.

For many years landfill, was the main, practical means for dealing with the problem of waste tires. However, landfilling of tires is declining as a disposal option, since tires do not degrade easily in landfills, they are bulky, taking up valuable landfill space and preventing waste compaction. Open dumping may result in accidental fires with high pollution emissions. In the EU countries in 1990 the percentage of tires discarded in landfills was 62% of all produced waste tires in 2000 about 35% and in 2006 (as it results from the EU legislation) this percentage will decrease to 0%. Some countries including the Slovak Republic have already banned the use of discarded tires for landfilling.

A low percentage of scrap tires are recycled with material recovery and reused for second-quality rubber products (see methods of recycling in the next chapter). The problem is that waste tire generation rate is much more important than the amount of material required for these alternative uses. Because of their high calorific value, waste tires have been used as fuel in rotary cement kilns. However, this process can be acceptable from an environmental point of view only in the case of controlled combustion due to the toxic emissions produced during the tire combustion processes.

The high volatile carbon content and heating value (33-35 MJ/kg[1]) make the scrap tires an excellent material for energy recovery. For this reason, both pyrolysis and combustion are currently receiving renewed attention. Pyrolysis offers an environmentally attractive method to decompose a wide range of wastes, including waste tires. In the pyrolysis process, the organic volatile matter of tires (around 60 wt%) is decomposed to low molecular weight products, liquids or gases, which can be used as fuels or chemicals source. The non-volatile carbon black and the inorganic components (around 40 wt%) remain as solid residues and can be recycled in other applications. Combustion of tires has been used also for generation of electrical energy. However, for minimizing emissions the conditions of the combustion process must be optimized.

In this paper a literature review of both pyrolysis and combustion processes of scrap tires is presented. All, the characteristics of materials, methods, effect of various process parameters, kinetic modelling applied to the pyrolysis and combustion of tires, characteristic of the products and emissions are reviewed.

2. Methods of recycling waste tires

The possible ways of recycling waste tires are as follows:

Retreading and reusing of tires:

In this process, the remaining tread is ground away from a tire to be remoulded and a new tread rubber strip is fused to the old carcass by vulcanization. The economic potential of the process is major advantage and the quality of the products is a disadvantage of retreading.

Recycling by production of ground rubber for use in other applications:

By mechanical or cryomechanical (cooling of rubber to a temperature ranging between –60 to –100°C) milling of tires the ground rubber of various sizes can be produced. These materials are used in other applications. For example: as component in asphalts, carpets, sport surfaces and children's playgrounds. By the cryomechanical technology it is possible to obtain a very fine powder, which can be used as reinforcement in new rubber products. Retaining of some properties of rubber materials and the absence of direct air emissions are the major advantages, However, the high consumption of energy, liquid nitrogen in the cryomechanical process and the limited market for the products are the main disadvantages of the process.

Reclaiming rubber raw materials:

Many attempts have been made since 1910 for reclaiming of scrap rubber products. However, rubber products during the processing and moulding are crosslinked, and therefore they cannot be again softened or remoulded by heating. Reclaiming of scrap rubber products means the conversion of a three dimensionally interlinked, insoluble and infusible strong thermoset polymer to a two dimensional, soft, plastic, processable and vulcanizable polymer simulating many of the properties of virgin rubber. In this case reclaiming of scrap rubber is more complicated than reclaiming of thermoplastics. Various methods and processes for reclaiming waste rubber were developed. The most important of them are: the mechanical shearing process[2], thermomechanical reclaiming[3], reclaiming by use of various chemical agents[4], microwave reclaiming[5], ultrasonic reclaiming[6], pyrolysis of waste rubber, reclaiming by renewable resource materials and reclaiming by biotechnological processes. A review of reclaiming waste rubber was published by Adhikari and Maiti[7].

The main problem which reclaim producers face is the acceptability of reclaim by rubber industry as a raw material. This depends upon two major factors:

- The quality of reclaim products measured by their properties compared to the properties of virgin raw materials,
- The cost of reclaim compared to the cost of virgin rubber.

Recycling of scrape tires by reclaiming needs further research to obtain better quality of reclaim and a more cost-effective reclaiming process.

Pyrolysis:

Tire pyrolysis (thermal decomposition in an oxygen-free environment) is currently receiving renewed attention. Recycling of tires by pyrolysis offers an environmentally attractive method. The products of the tire pyrolysis process are: Solid char (30-40 wt%), liquid residue (40-60 wt%), and gases (5-20 wt%).(see chapter 6). The solid residue contains carbon black and the mineral matter initially present in the tire. This solid char may be used as reinforcement in the rubber industry, as activated carbon or as smokeless fuel. The liquid product consists of a very complex mixture of organic components. Thus, the derived oils may be used directly as fuels, petroleum refinery feedstock or a source of chemicals. The gaseous fraction is composed of non-condensable organics as, H_2, H_2S, CO, CO_2, CH4, C_2H_4, C_3H_6 etc. The gas fraction can be used as fuel in the pyrolyses process.

For growing economical efficiency and enlargement of markets for pyrolysis products, further research is needed in the field of process conditions, optimisation, and product characterisation and treatment.

Combustion

Incineration

Waste tires can be used directly as fuels in the incinerators. Due to their high heating value scrap tires are excellent materials for energy recovery. The use of tires directly as fuel in incinerators has the following advantages: Reduced power-production costs, maximum heat recovery, environmentally acceptable process. The disadvantages are: no material recovery, large capital investment, need for flue gas cleaning, CO_2 emission, high operating costs. Scrap tires are used also as fuel in cement kilns. More research works is needed for obtaining environmental impacts of this process, especially from the view of polycyclic aromatic hydrocarbon (PAH) emissions.

3. Characteristics and composition of scrap tires

Tires are composed of rubber compounds and textile or steel cords. Rubber compounds generally consist of elastomers (natural or synthetic rubber), carbon black, hydrocarbon oils, zinc oxide, sulphur and sulphur compounds and other chemicals such as stabilizers, anti-oxidants, anti-ozonants, etc. Table 1 shows the proximate analysis of scrap tires declared by various authors. The elemental analysis of waste tires found in the literature is presented in Table 2.

Tires consist of various types of rubber compounds with different compositions. Due analysing different rubber compounds, various authors report different results of elemental analysis, as shown in Table 2. For obtaining the average content of elements in tires each part of tire must be analysed.

Table 1: Proximate analysis of scrap tire rubber

Author	Volatile (wt%)	Fixed carbon (wt%)	Moisture (wt%)	Ash (wt%)	Steel (wt%)
This paper	61.61	22.66	1.72	14.01	-
Rodrigues et al. [8] *	58.8	27.7	-	3.9	9.6
Jong Min Lee et al.[9]	67.3	28.5	0.5	3.7	-
Yu Min Chang et al.[10]	62.32	26.26	1.31	10.29	-
Gonzales et al. [11]	61.9	29.2	0.7	8.0	-
Chen et al. [12]	93.73 **	-	0.54	5.3	-
Loresgoiti et al. [13] *	59.3	27.6	-	3.5	9.6
Orr et al. [14]	68.7	23.3	0.4	7.6	-
Williams and Bottrill [15]	66.5	30.3	0.8	2.4	-
Atal and Levendis [16]	58.7	33.6	-	7.7	-

**- Based on reinforced tire with steel cords **- including fixed carbon*

Table 2: Elemental analysis of scrap tire rubber

Author	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%)	Ashes (inorganic)
This paper**	81.24	7.36	0.49	1.99	8.92	-
Rodrigues et al. [8] *	74.2	5.8	0.3	1.5	4.7	13.5
Jong Min Lee et al.[9]	83.8	7.6	0.4	1.4	3.1	3.7
Yu Min Chang et al.[10]	74.4	6.96	0.21	1.6	5.02	10.21
Gonzales et al. [11]	86.7	8.1	0.4	1.4	1.3	2.9
Chen et al. [12]	81.16	7.22	0.47	1.64	2.07	7.44
Berrueco et al. [17]	88.5	6.6	0.4	1.6	3.0	-
Arion et al. [18]	73.8	5.3	0.44	1.71	0.11	17.8
Loresgoiti et al. [13] *	74.2	5.8	0.3	1.5	5.1	13.1
Orr et al. [14]	81.3	7.3	0.3	1.5	-	1.4
Williams and Bottrill [15]	85.8	8.0	0.4	1.0	2.3	2.4
Lanoir et al. [19]	82.63	7.5	0.36	1.69	-	-
Senneca et al. [20]	86.7	6.9	0.3	1.9	1.0	3.3
Roy et al. [21]	86.6	8.1	0.5	0.8	2.2	-
Cunliffe and Williams [22]	86.4	8.0	0.5	1.7	3.4	2.4

**- Based on reinforced tire with steel cords **- Based on free of ash*

4. Pyrolysis and combustion methods and equipment

4.1 Thermal decomposition of scrap tire

A number of experimental apparatus and laboratory scale plants for pyrolysis and combustion of scrap tires was presented by various authors. The behaviour of the thermal decomposition of rubber is generally studied by thermogravimetry analysis. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) are used as standard methods for studying thermal degradation of waste rubber samples. From the thermogravimetry analysis provided by various authors (for example: Leung and Wang[23], Yang et al.[24], Berrueco et al.[17]) results that more than one degradation temperature region during rubber pyrolysis is recorded.

Measurements provided in our laboratory sustain this fact (see Figure 2), however, it depends upon the composition of rubber compounds. The measured TG curves show two different mass loss regions over a temperature range of 250-550°C. Based on the evaporating characteristics of individual rubber components at the temperature ranging from 250 to 380°C, additives, oils and plasticizers are lost. At the temperature ranging 400-550 NR, SBR and BR are decomposed. A typical behaviour of sample mass loss during pyrolysis and char combustion measured by TG in our laboratory is shown in Figure 1.

The start and end temperatures of the pyrolysis process reported by various authors are compared with our measurements in Table 3.

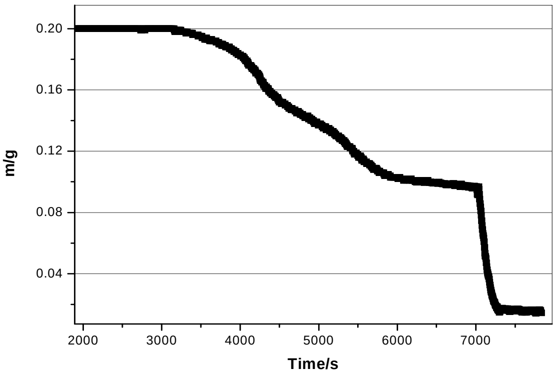

Figure 1. A typical behaviour of mass loss of a scrap tire sample during pyrolysis and char combustion

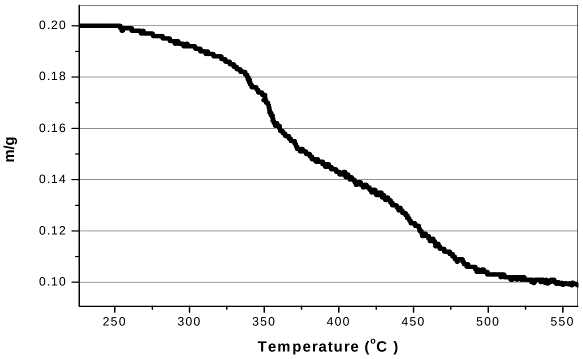

Figure 2: Degradation temperature regions of scrap tire pyrolysis

Table 3: Start and end temperatures of pyrolysis of scrap tires

Author	Start temperature of pyrolysis (°C)	End temperature of pyrolysis (°C)	Heating rate (°C/min)
This paper	250	550	5
Berrueco et al. [17]	200	500	15
Leung and Wang [23]	200	550	10
Chen et al. [12]	250	500	5
Senneca et al. [20]	200	450	5
Chen and Qian [25]	200	550	10
Conesa et al. [26]	250	500	5

4.2. Pyrolysis reactors

A number of studies has been done to investigate the pyrolysis of waste tires in both laboratory and industrial scale. Williams et al.[27] pyrolysed waste tires in a nitrogen atmosphere using a fixed-bed batch reactor at a temperature ranging from 300 to 720°C. This type reactor was also used by Berrueco et al[17], Cunliffe and Williams[22] and others. Rodriguez et al.[8], Murena et al.[28] and Laresgoti et al.[13] employed for pyrolysing waste tires autoclaves. Kaminsky and Mennerich[29] pyrolysed waste tires in a fluidized bed reactor at a temperature ranging from 500 to700°C. Roy et al.[21] used for the thermal decomposition of waste tires vacuum pyrolysis. Also plasma technology was employed by Tang and Huang[30] for pyrolysing waste tires.

4.3. Combustion technologies

Fluidized-bed combustion is one of the most appropriate process for the treatment of waste tires. However, high operating costs and considerable feedstock preparation make this process relatively expensive. Fluidized-bed reactor for waste tire combustion was used by a number of authors[31] [32] [33].

Rotary kiln combustion enables combustion of tires in different sizes with relatively low operating costs. The requirement of a post-combustion chamber and particulate filtration, for controlling emissions are disadvantages of combustion in rotary kiln combustors. Waste tire utilisation in cement kilns brings economical benefits. However, environmental impact of this process calls for more research, especially from the view of emissions of polycyclic aromatic hydrocarbons. Carraso et al.[34], reports that energy recovery of scrape tires used by a cement kiln meets environmental standards. Giugliano et al.[35] determined the influence of shredded tires on the combustion process in a cement kiln.

Combustion in grate kilns is also used for waste tire combustion. The use of combustion in the grate kiln technology is justified economically, especially for large-sized plants.

5. Process conditions

5.1. Pyrolysis

Pyrolysis of waste tires leads to the production of a solid carbon residue (char), a condensable fraction (pyro-oil) and gases. The percentage of each phase is influenced by process conditions, such as temperature, pressure, heating rate, particle sizes, heat exchange system, catalysis etc. Williams et. al.[27] pyrolysing waste tire at a temperature between 300 and 720°C and heating rates 5 and 80°C min^{-1} found that the maximum conversion of tire (see Table 4) occurred at a temperature of 600°C. Laresgoiti et al.[13] found that the temperature does not significantly influence the char and gas yields over 500°C. However, temperature variations influence the gas composition. Rodriguez et. al.[8] pyrolysed cross-section samples (2-3 cm wide), representative of whole tire, at 300-700°C. They report that Tire-pyrolysis liquids are a complex mixture of hydrocarbons, which contains 0.4% of N and 1.2% of S. About 30% of such liquids is an easily distillable fraction with boiling points (70-210°C) and about 60% of liquids have boiling point range of 150-370°C.

Berrueco et al.[17], analysed the temperature influence on the global yields and the gas composition. They observed that the liquid yield increases with temperature from 400 to 500°C. However at temperatures higher than 500°C, this parameter remained almost constant. The gas yield showed a growth from 2.4 wt% at 400°C to 4.4 wt% at 700°C. A different distribution of scrap tire into yields (char, liquid and gas) was reported by Chang[10] (30-53 wt% gas, 28-42 wt% oil and 14-28 wt%

char). Zabanioti and Stavropolos[38] pyrolysing scrap tire in a helium atmosphere in the temperature range 390-890^{o}C and heating rates of 70-90^{o}C. min $^{-1}$found out that the char yield decreases with temperature reaching an asymptotic value of 20 wt% of raw material, at about 830^{o}C. The gas yield (condensable and non condensable) increases with temperature reaching an asymptotic value of 73 wt.% of raw material, at about 830^{o}C. Barobboti et al.[39] pyrolysed scrap tires in temperature range of 400-460^{o}C, nitrogen flow rate of 02-0.5 m^{3}h^{-1} and particle size of 2-20 mm. As optimum conditions they present 430^{o}C, 0.35 m^{3}h^{-1} and 10 mm, respectively. At this conditions the yield of char and liquid were 32.5 and 51.0 wt.%, respectively.

Lee et al.[9] studied pyrolysis of waste tires with partial oxidation in a fluidized-bed reactor. They found that with increasing O_2 concentration, the gas yield increases from 22 to 43 % since CO_2 generation increases. Energy recovery is about 0.32 with O_2 concentrations up to, 6.5 %, thereafter, energy recovery is reduced to 0.24. Murena et al. carried out hydrogenative pyrolysis of waste tires for better saturation of the brocken bonds. They declared that hydrogenative pyrolysis enables the use of the lowest reaction temperatures 390-430^{o}C, the production of solid residue is minimized and the production of liquid phase is maximized. Roy et al.[40] pyrolysed tire rubber at 500°C and a total pressure varying between 0.8 and 28.0 kPa. They found that the yields of gas, oil and pyrolytic carbon black changed little with the pyrolysis pressure. However, the oil composition and the carbon black characteristics depended considerably on the pyrolysis pressure.

The influence of some process conditions on char, liquid and gas yields presented by different authors is shown in Table 4.

Table 4: Influence of some process conditions on char, liquid and gas yields presented by different authors

Author	Temperature (^{o}C)	Heating rate (^{o}C/min)	Pressure kPa	Sample sizes	Solid (wt.%)	Liquid (wt %)	Gas (wt.%)
Williams et al. [27]	300-720	5-50	101	-	35	55	10
Laresgoiti et al. [37]	400-700	15	101	20-30 mm	43-53	28-40	7-9
Berrueco et al. [17]	400-700	15	101	20 mm	47-63	30-43	2.4-4.4
González et al. [11]	350-700	5-20	101	0.2-1.6 mm	37-40	55	4-11
Pakdel et al. [41]	440-570	I	1.3-28	3.8 cm^{3}	30.6-53.4	50-60	3.2-11.9
Barbooti et al [39]	400-460	-	101	2-20 mm	32.5	51.0	16.6
Chang [10]	200-600	I	101	20 mg	14-28	28-42	30-53
Cunliffe and Williams [22]	450-60	-	101	-	37-38	53-58	5-9
Roy et al. [40]	25-500	15	0.8-28	-	35-36	62	1-3

5. 2. Combustion

Both combustion behaviour and emissions from the combustion process of waste tires are influenced by process conditions such as temperature, oxygen enrichment, particle sizes, reactor type, etc. Using thermogravimetry analysis Atal and Levendis[16] observed that tire particles experienced an intense primary volatile combustion phase, followed by a phase of simultaneous secondary volatile combustion of less intensity and char combustion. They also found out that char burnout times were considerably shorter for tire particles than for coal. Mastral et al.[42] using fluidized-bed combustion reported that both gas superficial velocity and partial pressure of oxygen exert influence upon the overall fixed carbon combustion efficiency. The efficiency increases slightly with the oxygen concentration and significantly if the gas superficial velocity decreases. They also burned waste tires in an atmospheric fluidized bed combustion plant with an airflow of 860 'l/h and 20% excess oxygen at three' different combustion temperatures. (750, 850, and 950°C). They observed that the introduction of tires in the feeder increases the total PAH amount emitted with respect to coal emissions, with minimal variations at the combustion temperatures studied by them: thus, the higher the temperature, the lower the amount of emitted polycyclic aromatic hydrocarbons.

Courtemanche et al. [43] burned coal and waste tire crumb in an electrically heated drop-tube furnace at high particle heating rates (10^{4}-10^{5} K s^{-1}) and elevated gas temperatures (1300–1600 K). They found that combustion of coal generated four times more NO_x than combustion of tire crumb, in proportion to their nitrogen content.

A complex study of process conditions such as temperature, O_2 concentration and particle sizes on combustion behaviour and pollutant emissions was not found in the literature. For disposal of waste tires by combustion with minimum environmental impact also for the prevention of fire hazards in tire landfills, more research in this area is required.

6. Characteristics and composition of the pyrolysis products

Use of pyrolysis as a method for recycling waste tire depends on the market for pyrolysis products. For this reason, characterization of pyrolysis products and possibilities of their application in other processes is very important. At present time, the main application for solid char is its use as active carbon, as reinforcement in rubber industry and as smokeless fuel. The liquid product is used as a fuel, or a source of chemicals, and the gas fraction as a fuel in the pyrolyses process.

6.1. Solid residue

The solid residue contains carbon black and the mineral matter initially present in the tire. Several studies have reported the production of chars and active carbon from waste tires [44], [45]. These active carbons have been used to adsorb phenols, basic dyes and metals, phenols, butane and natural gas. Active carbon from solid product of pyrolysis process is produced by activation with an activating gas at 800-100°C. Carbon characteristics (especially specific area) are greatly influenced by the degree of the activation also by nature of activating agent (steam or CO_2) and process temperature. Based on the current technology and literature results tire chare activation below 700°C looks impractical [44]. The particle size of the tire rubber was found to have influence on the porosity of the resultant carbon generated from steam activation[44].

Elemental analysis carried out by Zabaniotou et. al.[45] shows that pyrolysis char contains 71 wt.% of C, 13.3% wt. of O, 5.4 wt.% of Fe, 2.8 wt.% of S, 2.3 wt.% of Zn, 1.3 wt.% of Ca, and 0.3 wt.% of Al.

6.2. Pyrolysis liquid product

The liquid phase is the most important product of tire pyrolysis process. There are several papers in the literature devoted to the study of the characteristics of pyrolysis liquid products.[8] [13] [15] [46] [47]. Gas chromatography/Mass spectroscopy (GC/MS) is the most often method used not only for analysing pyrolysis liquid product, but also for analysing the gas yield and products of char combustion. Laresgoiti et al.[13], present a detailed characterization of the all pyrolysis liquids obtained at 300, 400, 500, 600, and 700°C. All, the GC/MS analysis, elemental analysis, gross calorific values and distillation data were studied. They report that tire derived liquids are a complex mixture of C_6-C_{24} organic compounds, containing a lot of aromatics (53.4–74.8%), some nitrogenated (2.47–3.5%) and some oxygenated compounds (2.29–4.85%). Their GCV (42 MJ kg^{-1}) is even higher than that specified for commercial heating oils, but the sulphur content (1–1.4%) is close to or slightly over the limit value. Significant quantities of valuable light hydrocarbons such as benzene, toluene, xylene, limonene, etc. were obtained. The concentration of these compounds increases with temperature up to 500°C and then decreases. There is also an important portion of polycyclic aromatics, such as naphthalenes, phenanthrenes, fluorenes, diphenlys, etc.; their concentration as well as that of total aromatics increase significantly with temperature.

Pakdel et. al.[41] reports that vacuum pyrolysis of used tires produces approximately 55 wt.% of pyrolysis oil. This oil typically contains 20-25 wt.% of naphtha fraction with a boiling point lower than 200°C. The naphtha fraction typically contains 20-25 wt. % *dl*- limonene. Williams and Taylor[48], found that the pyrolytic oil had molecular weight range from a nominal 50 to 1200.

6. 3. Pyrolysis gases

The yield of the gas fraction obtained in different experimental systems shows important variations. For example: Berrueco et. al.[17] obtained the gas yield 2.4-4.4 wt.%, but Chang [10] 30-53 wt.%. Laresgoiti et al.[37], using an autoclave in a nitrogen atmosphere at temperatures between 400 and 700 C, found that the pyrolyzed gases consisted of CO, CO_2, H_2S and hydrocarbons such as CH_4, C_2H_4, C_3H_6 and C_4H_8, and their unsaturated derivatives. Berrueco et. al. [17] analysing pyrolysis gases by gas chromatography, found that the main gases produced by the pyrolysis process are H_2, CO, CO_2 and hydrocarbons: CH_4, C_2H_4, C_3H_6 and C_4H_8. Roy et al.[40] obtained gases by vacuum pyrolysis, mainly composed of H_2, CO, CO_2 and a few hydrocarbon gases. In general, main components of pyrolysis gases was reported by various authors as: H_2, H_2S, CO, CO_2, CH4, C_2H_4, C_3H_6 and other light hydrocarbons.

7. Pyrolysis and combustion kinetics

Several authors presented kinetic models for pyrolysis scrap tires[12][20] 23][49][50]. In general, these models are based on thermogravimetry data and Arrhenius equation and divide the decomposition of tires into two or more steps. The first order reaction based on the Arrhenius theory is commonly assumed by researchers in the kinetic analysis of data for tire decomposition:

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

In this equation *k* is the rate constant; *A* is the pre-exponential factor, *E* is the activation energy, *R* and *T* are the universal gas constant and absolute temperature, respectively. The rate of decomposition may be expressed by:

$$\frac{d\alpha}{dt} = k\left(1-\alpha\right)^n \tag{2}$$

where α is the fraction of reactant decomposed at time *t* and *n* is the order of reaction

Some models published in the literature, which are the modification of the above given equations for tire pyrolysis under various conditions, together with experimental conditions and obtained kinetic parameters are given below:

Leung and Wang ***[23]***:
Model:

$$\frac{d\alpha_T}{dt} = \sum_{i=1}^{3}\frac{d\alpha_i}{dt} = \sum_{i=1}^{3} A_i \exp\left(-\frac{E_i}{RT}\right)\left(1-\alpha\right) \tag{3}$$

where

α_T (min^{-1})- normalized mass loss rate, *A* - pre-exponential factor; *E* - activation energy; *R* - ideal gas constant *T* - absolute temperature, *t*- time, index (i=1.2,3) - reaction.

Experimental conditions:
Temperature: 20-600°C, particle size: 0.355- 0.425 mm, heating rate: 10-60°C/min used mobile gas: N_2. The kinetic parameters obtained are shown in the Table 5.

Table 5: Kinetic parameters obtained by Leung and Wang[23]

Heating rate	Activation energy, *E* (kJ/mol)		pre- exponential factor, *A*		Reaction order, *n*	
	Lower temperature	Higher temperature	Lower temperature	Higher temperature	Lower temperature	Higher temperature
10	164.5	136.1	6.29×10^{13}	2.31×10^{9}	1	1
30	180.9	133.6	1.32×10^{14}	2.09×10^{9}	1	1
45	203.4	107.0	7.58×10^{15}	3.34×10^{7}	1	1
60	218.7	99.1	1.13×10^{17}	1.02×10^{7}	1	1

Yang et. al ***[51]***:
Model:

$$\frac{d\alpha}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right)\left(1-\alpha\right)^n \tag{4}$$

where

α - mass fraction of the volatiles emitted at time *t*, *A* - pre-exponential factor; *E* - activation energy; *R* - ideal gas constant *T* - absolute temperature, *t*- time index (i=1.2,3)- reaction.

Experimental conditions:
Temperature: 30-550°C, sample weight: 4-8 mg, heating rate: 1- 40°C/min. used mobile gas: N_2. The kinetic parameters obtained are shown in the Table 6.

Table 6:The kinetic parameters obtained by Yang et al.[51]

Heating rate	Activation energy, *E* (kJ/mol)		pre- exponential factor, *A*		Reaction order, *n*	
	NR	SBR	NR	SBR	NR	SBR
1	207	152	3.89×10^{16}	5.44×10^{10}	2	2
10	207	152	2.36×10^{16}	4.15×10^{10}	1	1
40	-	139	-	8.82×10^{9}	1	1

Williams and Besler[52]:
Model:

$$\frac{dw}{dt} = -k\left(W - W_f\right) \tag{5}$$

where
W is the weight of sample at time *t*; W_f is the weight of residue at the end of the reaction, and *k* represens the rate constant defined by Arrhenius equation

Experimental conditions:
Temperature: 720°C, Sample sizes: <1 mm, heating rate: 5°C/min. used mobile gas: N_2
The kinetic parameters obtained are shown in the Table 7.

Table 7:The kinetic parameters obtained by Williams and Besler[52]

Heating rate	Activation energy, *E* (kJ/mol)		pre- exponential factor, *A*		Reaction order, *n*	
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B
5	142.7	120.8, 145.0	2.1×10^{8}	9.3×10^{7}, 1.1×10^{8}	-	-
20	90.8	128.3, 137.7	2.6×10^{4}	3.3×10^{5}, 2.1×10^{8}	-	-
40	70.4	66.1, 136.2	1.3×10^{3}	5.9×10^{2}, 6.3×10^{7}	-	-
80	66.4	55.6	1.1×10^{3}	1.3×10^{2}	-	-

A relatively small number of works devoted to the kinetics of combustion was found. Conesa et al.[50] modelled the combustion of tire rubber by dividing the decomposition process into pyrolysis and combustion steps. The pyrolysis step model assumes three independent organic fractions that are decomposed. For pyrolysis reactions the kinetic equation for the total mass loss is presented as:

$$\frac{dw}{dt} = \sum k_0 \exp\left(-\frac{E_i}{RT}\right) w_i^{\,n} \tag{6}$$

where *w* - mass fraction index i= 1,2,3 represents the fraction decomposed, k_0i - pre-exponential factor; *E* - activation energy; *R* - ideal gas constant *T* - absolute temperature and *t*- time. For fourth carbonaceous fraction an n-order reaction, with dependence on the oxygen partial pressure is used:

$$\frac{dw_4}{dt} = \sum k_{04} \exp\left(-\frac{E_4}{RT}\right) w_4^{\,n} p_{O_2}^{m} \tag{7}$$

The following parameters for this model were estimated by authors [50]:

	F1	F2	F3	F4
k_0	$2.84\text{x}10^6$	$2.64\text{x}10^{14}$	$4.15\text{x}10^{14}$	$3.79\text{x}10^8$
E (kJ/mol)	83.6	245.6	201.7	223.2
n	2.445	3.905	1.456	0.692
m	-	-	-	0.886

Leung and Wang[23] using the model described above (equation 3) for tire rubber char combustion determined following kinetic parameters:

Sample size mesh	Temperature (°C)	Activation energy, *E* (kJ/mol)	pre- exponential factor, *A*	Reaction order, *n*
8-16	45-610	145.4	$2.89\text{x}10^8$	1
16	450-620	148.1	$3.84\text{x}10^8$	1
40	450-620	161.2	$3.93\text{x}10^9$	1

8. Emissions from the combustion of tires

For disposal of waste tires by combustion and energy recovery the characteristics of emissions are the main factor, which must be studied. The amount of toxic emissions like SO_2, NO_x, CO and PAHs is affected by the process conditions and the technology used. Though emission characteristics of waste tire combustion have been studied by a number of authors, more research in this field is required.

Levendis et al.[53] comparing combustion of coal and waste rubber found that NO_x emissions from tires is 3-4 times lower than those from coal, emissions of SO_2 where comparable. CO and PAH emission yields from tire derived fuel were much higher than those from coal, but the relative amounts of individual PAH components were remarkable similar in the combustion effluent of the two fuels. Mastral, et al.[42] report that thus, the higher the temperature, the lower amount of emitted polycyclic aromatic hydrocarbons measured by fluidezed-bed combustion of waste tires. Lemieux et al.[54] reviewed Emissions of organic air toxics from open burning of various types of wastes. From this review results that PAH emissions were highest when combustion of polymers was taking place. For this reason a post-combustion chamber and particulate filtration, for controlling emissions from the tire combustion is required. In addition, the conditions of the combustion process must be optimized.

9. Conclusion

In this paper the current status of research devoted to the pyrolysis and combustion of scrap tires is presented. From the published works results that scrap tire rubber consists of about 60 wt.% volatile organics, 30 wt.% fixed carbon and 10 wt. % ash. Elemental analysis shows that the tire rubber contains approximately 80 wt.% C, 7 wt. H, 0.4 wt.% N, 1.5 wt.% S, 3 wt.% O and 8 wt.% ash. From thermogravimetry analysis provided by various authors results that pyrolysis of tire rubber at atmospheric pressure starts at a temperature of about 250°C and finishes at a temperature of around 550°C. Generally, more than one degradation temperature region during rubber pyrolysis is recorded. This fact also results from the thermogravimetric analysis made in our laboratory.

Several works have been devoted to the pyrolysis yield and their characteristics. However, pyrolysis yields and characteristics of the products obtained depend not only on the character of feed and operating conditions, but also on the specific characteristics of the system used. Therefore, results from different authors are different and difficult to compare. In general, three fractions are obtained. The solid residue (about 40 wt.%), liquid fraction (about 50 wt.%) and gas fraction (about 10 wt.%). Influence of the process conditions on the amount and characteristics of individual fractions was studied by the authors only partially. The general trend is an increase of yields to liquid and gas as the temperature increases.

From the works devoted to tire pyrolysis, which are focused on the generation of liquid fuel results that derived liquids are a complex mixture of organic compounds with a lot of aromatics. This liquid can be separated to light and higher fractions. The main components of pyrolysis gases reported by various authors are: H_2, H_2S, CO, CO_2, CH4, C_2H_4, C_3H_6 and other light hydrocarbons.

The results of kinetic modelling of scrap tire pyrolysis and combustion show large differences in the values of kinetic parameters obtained by different authors. However, these models generated good correlation between model and experimental data in the same work.

As main pollutants from the combustion of waste tires are reported: SO_2, NO_x, CO and PAHs. However, emissions from both the direct combustion of the waste tire and the combustion of tire pyrolysis products need more studies.

There is a significant demand for optimization of pyrolysis process conditions, more intense study of the influence of various factors on the pyrolysis products yields and characteristics, and also influence of operating parameters on energy recovery in a pyrolysis plant.

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