

The Effect of Temperature and Particle Size on the Pyrolysis Products of Waste Tires and the Formation Mechanism of Limonene

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Abstract. *The rapid development of the automotive industry has led to the accumulation of a large number of waste tires that contain a lot of reusable energy. Macromolecular organics in waste tires can be crack small molecule organics via pyrolysis. In this experiment, thermogravimetry (TG) and pyrolyzer-gas chromatography/mass spectrometry (PY-GC/MS) were used to study the pyrolysis behavior of waste tires with different particle sizes, and the effect of temperature and particle size on the pyrolysis products of waste tires under low-temperature pyrolysis conditions, respectively. The volatile substances in waste tires decomposed intensively at 300-500°C and were completely pyrolyzed at 500°C. The content of limonene in the pyrolysis product was significant, and the yield of limonene could reach 27.73% when the waste tire particles were 0.180-0.250 mm and the pyrolysis temperature was 380°C. The mechanism of limonene formation from waste tires was discussed. This study indicated that raw material particle sizes and pyrolysis temperature could change the components and content of pyrolysis products.*

Keyword: *waster tire, pyrolysis, particle size, pyrolysis temperature, limonene*

1. Introduction

The improvement of life standard among others has promoted automobile production and increased the number of waste tires. In 2019, the number of waste car tires in China were estimated at 330 million, this output rank is the first place in the world. China has promulgated a series of policy decrees but has not yet established a complete recycling system for waste tires, which incompletely resolved the accumulation of waste tires. Improper disposal of waste tires is not only wasting rubber resources but also harmful for human health and the environment [1].

The methods of waste tire treatment contain tire retreading, combustion, landfilling and pyrolysis, etc [1]. Only 10% of waste tires can be used for tire retreading in 2010 [2]. Combustion waste tires may lead to the release of some toxic and harmful substances, e.g., H₂S, polycyclic aromatic hydrocarbon (PHA) [1, 3]. Waste tires landfill would take up a lot of land resources, adversely affect the long-term settlement and restoration of soil [4-6]. The above methods to treat waste tire is not as an energy resource [7]. In the past decade, pyrolysis could maximize the conversion of waste tires into high-value products is a research subject that researchers focused densely on [8]. Pyrolysis refers to the chemical process of converting rubber into carbon black, high-value fuel oil and fuel gas in the absence of oxygen or the presence of inert gas. This is a high potential, attractively and environmentally friendly method to treat solid waste, which conforms with the principles of reduction, decontamination, treatment and recycling of waste tires [9].

The pyrolysis gas mainly includes ethylene, propylene, butene and isobutylene, the heating value is about 30-40 MJ Nm⁻³, and its energy can be used for the pyrolysis process and other applications [1,10]. The solid product is mainly carbon black, whose yield decreases with increasing temperature, and is about 32.4 wt% at 500°C [5]. Carbon black can be further processed to be used as activated carbon

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or reinforcing filler [11, 12]. Pyrolysis oil is mainly composed of paraffin, olefins and aromatic hydrocarbons. It also has the potential to be a substitute fuel for diesel and gasoline [6, 10]. In addition, pyrolysis products could be reprocessed into light aromatic compounds such as benzene, toluene, xylene and limonene, which have higher market value [13]. The limonene (1-methyl-4-(1-methylethenyl)-cyclohexene) in the product is a monoterpene unsaturated hydrocarbon as well as a high-value light hydrocarbon. Limonene can be used as synthetic terpene resin, pressure-sensitive adhesive and hot melt adhesive [14]. Limonene is a kind of widely used green organic solvent, which can be used as a water-insoluble solvent, insecticide, etc.; because it has antibacterial activity, antioxidant activity, antitumor activity, anti-cough effect and promotes the role of bile secretion in the dissolution of gallstones in the gallbladder, which can be used to treat different types of cancer in the medical field; it acts as an antioxidant, preservative and perfume additive in food additives, and can also be used in the synthesis of phase carvone and menthol. Natural plant oils contain limonene, which can be obtained by pressing, steam distillation, supercritical extraction, etc., and the source of raw materials is relatively single [14-16]. The recovery of limonene from the pyrolysis product can make the pyrolysis product more economically valuable.

The pyrolysis product distribution of the waste tire depends on the pyrolysis raw material, particle size, pyrolysis temperature, pyrolysis pressure, catalyst, residence time and carrier gas flow rate [17]. The increase of the pyrolysis temperature has a great influence on the type and content of the pyrolysis product, it also causes the secondary reaction of the pyrolysis product and the decomposition of the inorganic substance [11]. Olefin compounds are further converted into aromatic hydrocarbons through the decomposition of double bonds at a pyrolysis temperature higher than 390°C [18]. As temperature rises, the initial pyrolysis products will continue to crack into small molecules, and the pyrolysis gas yield will increase, leading the content of pyrolysis oil to reduce [19]. The increase of particle size affects the temperature distribution inside the particles, the time for complete release of volatiles and the overall pyrolysis rate [20, 21].

At pyrolysis temperature lower than 500°C, there are few studies on the effect of particle size on pyrolysis products. The target product content is maximized by exploring the proper choice of temperature and particle size. In this investigation, the element content in the waste tire was analyzed by the element analyzer. The effects of temperature and particle size on the pyrolysis behavior of tires and the pyrolysis products were studied. Further, the formation mechanism and process conditions of limonene were explored.

2. Material and methods

2.1 Material preparation

The used waste tires came from a waste tire recycling station in the city of Qingdao, China. Waste tires were mainly car tires made of natural rubber. First, the waste tires were crushed into small pieces to removed steel wire and other non-rubber materials, then the tire particles were divided into six particles size fractions, i.e.; (>0.850 mm (>20 mesh), 0.425-0.850 mm (20-40 mesh), 0.250-0.425 mm (40-60 mesh), 0.180-0.250 mm (60-80 mesh), 0.150-0.180 mm (80-100 mesh) and <0.150 mm (<100 mesh)) through different sizes of meshes (Taylor Standard Sieve). The tire particles were dried in an oven at 40°C for 4 h [6].

2.2 Element analysis and proximate analysis

The content of carbon(C), hydrogen(H), nitrogen(N), sulfur(S) in the waste tires was obtained by a CHNS/O analyzer (Vario Micro cube, Elementar) and measured according to JJF 1321-2011. The percentage of oxygen(O) was calculated by the difference in the waste tires. The content of moisture (M), ash (A) and volatile matter (VM) was measured by ASTM D3173-11, ASTM D3174-02 and ASTM D3175-07 standards respectively. The samples were weighed at 1.00 ± 0.01 mg by using electronic balance and triplicated each time, which was dried in an oven at 500°C for 1 h and cooled to room temperature, the weight loss before and after drying was moisture; which was dried in a muffle furnace

at 500°C for 1 h, heat at 900°C for 3 h, and cool to room temperature, the weight of the remaining sample in the crucible was the weight of ash; which was heated in a muffle furnace at 930°C for 7 min, and cooled to room temperature in a desiccator, the weight loss before and after heating was the weight of volatiles and moisture. Fixed carbon (FC) was calculated by the formula (1) [7].

$$FC = 100\% - M - VM - A \quad (1)$$

2.3 Thermogravimetric analysis

The thermogravimetry (TG) method was used to explore the relationship between the weight of matter and temperature to study the thermal stability of investigated materials. The TG was tested via the thermal analyzer (Q500, TA Instruments, USA). The thermal analyzer was increased from room temperature to approximately 700°C at a heating rate of 20°C min⁻¹. The experiment was run in a nitrogen atmosphere with a flow rate of 100 mL min⁻¹. The tire particles were added into the alumina crucible of 6.00±0.01 mg. The real-time changes of the weight were monitored throughout the pyrolysis process [4].

2.4 Pyrolizer-gas chromatography/mass spectrometer system

The entire system of pyrolizer-gas chromatography/mass spectrometer (PY-GC/MS) was made of a pyrolizer (EGA/PY3030D, Frontier, Japan) and a gas chromatography/mass spectrometer (GC/MS-QP2010, Shimadzu, Japan). The pyrolizer was coupled with the GC/MS to separate the compounds liberated [10,22]. A Rxi-5silMS column (30 m-0.25 mm-0.25 µm) was applied in the GC/MS system. The GC/MS program was set as follows: The transfer line (between gas-chromatograph and the mass spectrometer) temperature, ion source temperature and inlet temperature were held at 300°C, 250°C and 330°C, respectively. Under the condition that the heating rate was 5°C min⁻¹, the column temperature was kept at 40°C, 130°C and 310°C for 3 min, 1 min and 10 min respectively. High-purity helium was used as a carrier gas to pass into the reaction system at a flow rate of 1.75 mL min⁻¹.

2.5 PY-GC/MS experimental procedure

In the experiments, three different pyrolysis temperatures of 200°C, 380°C and 500°C, i. e. corresponding to the initial pyrolysis temperature, maximum weight loss pyrolysis temperature, and the final pyrolysis temperature, respectively, were taken into account. About 2.00 ± 0.01 mg of the tire particles were loaded in the crucible each time. The crucible was diverted into the pyrolizer when the pyrolizer reached the desired temperature, and the detected volatiles was identified by comparing the mass spectrum library connected to the PY-GC/MS instrument [22, 23]. In the experiment, an already mentioned helium was used as the carrier gas, and it was passed into the pyrolizer in advance to create an oxygen-free experimental environment.

3. Results and discussions

3.1 Element analysis and proximate analysis

The elemental composition of waste tires is very important, as the wt% or amounts of elements existent in the waste tire can influence pyrolysis rate and the amounts of pyrolysis product [5,10]. The wt% of C, H, N, S and O in tires of different particle sizes is listed in Table 1. The proximate analysis of waste tires is tabulated in Table 2. When the particle size was greater than 0.150 mm, the content of C, H, A, VM and FC was about 80%, 8%, 7%, 63% and 25% respectively. These were very similar to previous research [7]. But when the particle size was less than 0.150 mm, the content of C and H was the lowest, 70.85% and 6.83%, respectively, and the content of A was up to 18.29%. According to Wang et al. [5], the C, H and A content of the tire tread rubber was 56.6%, 6.8%, and 18.04% respectively. Therefore it was speculated that most of the tire particles with a particle size of less than 0.150 mm belong to the tire tread rubber in the study. It may also be that inorganic components are more likely to be broken into small molecular substances, resulting in a higher A content and lower C content of the

particle size <0.150 mm. The sulfur content found in tire particles was due to the vulcanization process, this was related to the addition of sulfur in the tire manufacturing process [7, 24].

Table 1. Elemental analysis of tire in different particle size ranges

Size (mm)	Elemental analysis (wt%)				
	N	C	H	S	O
>0.850	0.47±0.23	79.88±0.46	8.51±0.26	0.99±0.05	2.94±0.96
0.425-0.850	0.55±0.32	80.37±0.85	7.87±0.19	1.31±0.02	2.52±0.81
0.250-0.425	0.55±0.44	80.5±1.22	7.73±0.38	1.17±0.13	2.53±0.88
0.180-0.250	0.68±0.23	80.71±0.98	7.61±0.46	1.16±0.08	2.44±0.59
0.150-0.180	0.59±0.27	80.07±1.02	7.56±0.28	1.17±0.14	2.62±0.82
<0.150	0.56±0.35	70.85±0.58	6.83±0.39	1.07±0.06	3.92±0.27

Table 2. Proximate analysis of tire in different particle size ranges

Size(mm)	Proximate analysis(wt%)			
	M	A	VM	FC
>0.850	4.38±0.03	7.93±0.8	62.95±0.07	24.74±0.36
0.425-0.850	4.23±0.05	6.67±0.6	62.63±0.03	26.47±0.48
0.250-0.425	4.48±0.02	6.24±0.5	64.14±0.04	25.14±0.52
0.180-0.250	3.57±0.04	7.26±0.5	63.49±0.03	25.68±0.34
0.150-0.180	3.50±0.04	9.16±1.2	62.51±0.03	24.83±0.46
<0.150	4.10±0.03	18.29±2.5	50.55±0.04	27.06±0.49

M: Moisture; A: Ash; VM: Volatile matter; FC: Fixed carbon; C: Carbon; H: Hydrogen (includes the hydrogen from water); N: Nitrogen; S: Sulfur.

3.2 TG and GC/MS analysis

The curves of TG and derivative thermogravimetry (DTG) for particle size of >0.850 mm, 0.425-0.850 mm, 0.250-0.425 mm, 0.185-0.250 mm, 0.150-0.180 mm and <0.150 mm with the increase of temperature is shown in Figure 1(a) and (b), respectively. Using the same particle size, tire pyrolysis could be divided into three stages according to the TG and DTG curves, i.e.; the initial pyrolysis temperature (100-300°C), maximum weight loss pyrolysis temperature (300-500°C), and the final pyrolysis temperature (500-680°C). TG reflected the weight loss rate of the tire was about 6.15% in the first pyrolysis temperature range. In this stage, the structure of the tire was relatively stable, plasticizers were decomposed, and the tires lose weight slowly [25]. During the maximum weight loss pyrolysis temperature stage, the TG curve drops rapidly (66.71% and 54.65%, depending on the particle size), and the tire components were rapidly decomposed. This was attributed to the high content of volatiles in the tire and the appearance of concentrated volatilization at 300-500°C [11]. In the final pyrolysis temperature range, the synthetic rubber was completely decomposed. When the temperature was higher than 500°C, the weight was relatively stable, and under this condition, a polycondensation reaction mainly occurred. It was discovered that the thermal decomposition started at 300°C and almost was completed at 500°C, which was consistent with the temperature decomposition range of the tire [5,8,26]. DTG represents the connection between the speed of weight loss and temperature. Compared with the TG curve, the DTG curve can observe the degradation rate more clearly [17]. Generally, the higher the DTG value, the faster is the degradation rate. In Figure 1(b), the peak of DTG appeared at 300-500°C, which is the decomposition behavior of tires because of the rubber in the tires. Simultaneously, this was consistent with the previous study on the decomposition temperature range of natural rubber and synthetic rubber [5, 25]. According to Figure 1(a, b), the three pyrolysis temperatures of initial pyrolysis (200°C), maximum weight loss rate pyrolysis (380°C) and final pyrolysis (500°C) were selected for further study.

When the particle size was less than 0.150 mm, the weight loss was only 54.65% (Figure 1a), and the DTA peak value was lower than for others particle sizes. It was speculated that this phenomenon was caused by lower rubber content in tire particles. The proximate analysis showing that the VM content of tire particles with particle size less than 0.150 mm was lower confirms this presumption.

The GC/MS analysis results of the products of different tire particle sizes at the three pyrolysis temperatures determined by TG analysis are shown in Table 3. The characteristic peaks identification was done by the PBM (Probability Based Matching) algorithm on their spectra [10]. The organic matters that complete the matching were classified according to functional groups and their contents were counted. The type of organic matters in the pyrolysis product increases first and then decreases with the rise of temperature, which is consistent with the analysis results of the TG and DTG curves, shown in Figure 1. The temperature rise was conducive to the progress of the pyrolysis reaction. The higher the temperature, the more secondary reaction can be observed [19].

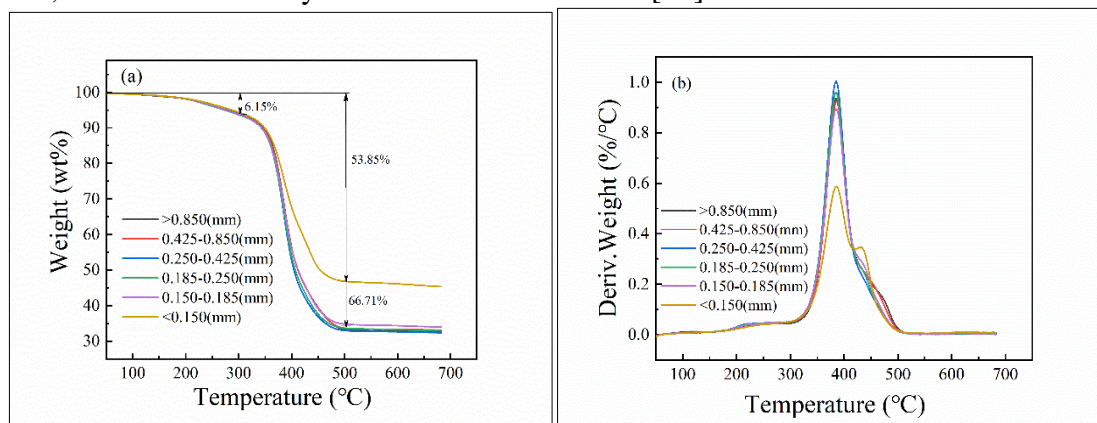


Figure 1. Profile of the a) thermogravimetry (TG) and b) derivative thermogravimetry (DTG) of waste tire particles of different particle sizes, 20°C min⁻¹ temperature rate

3.3 Effect of pyrolysis temperature on pyrolysis products

Temperature is one of the critical parameters affecting the pyrolysis product yield, as well as heat transfer efficiency, pyrolysis-driven events, and the energy required for pyrolysis [11,27]. In the pyrolysis experiment, the method adopted was to complete the heating process before materials feeding, so that the heating rate would have no effect. The pyrolysis products at 200°C, 380°C and 500°C were studied. The types of organic components in the pyrolysis products and the weight loss of tire particles at different pyrolysis temperatures are listed in Table 3. As the pyrolysis temperature was set at 200°C, 380°C and 500°C, the number of organic components included 28±6, 74±10, 33±5, respectively. This indicates depending on the particle size that temperature had a significant influence on the types of pyrolysis products. When the temperature was lower than 300°C, the tire pyrolysis was incomplete, and the rest of the tires was in a state of heterogeneous adhesiveness [7]. According to the thermal analysis, when the pyrolysis temperature was 380°C, the volatilization rate of volatiles in tire particles was the fastest. The macromolecules in the tire rubber undergo depolymerization and fragmentation and continue to crack into small molecules with the smaller molecular weight with the rise of temperature [28]. In addition, in the pyrolysis product would occur secondary re-polymerization or carbonization reactions under the pyrolysis condition of 500°C [7].

The main organic components were determined at the pyrolysis temperature of 200°C (Table 4), 380°C (Table 5) and 500°C (Table 6). In the same particle size range, the pyrolysis products mainly included alcohols, nitrogen compounds, acids, esters, and alkanes at the pyrolysis temperature of 200°C. Pyrolysis products were composed of limonene, olefins, benzenes, alcohols, acids, esters, alkanes, ketones and halogen-containing substances, at 380°C pyrolysis temperature. When the tire particles were pyrolyzed at 500°C, the pyrolysis products could be mainly divided into olefins, benzenes, alcohols, alkanes, halogen-containing substances and sulfur-containing compounds. Maximum nitrogenous substance content (about 50%) was obtained at 200°C. Combined with TG analysis, it is presumed that this result was observed because the additive in the tire was mainly pyrolyzed at this temperature [5]. The content of nitrogenous substances was very closely related to the pyrolysis temperature, but a direct relationship with the content of nitrogen has not been observed. When the pyrolysis temperature was

380°C, the maximum content of aliphatic compounds was 97.62%, of which above 60% were olefins. This fact can be related to the unsaturated nature of the polymer contained in the tire. The content of benzene species increased from $4.55 \pm 0.50\%$ at 380°C to $15.05 \pm 13.25\%$ at 500°C. The increase in the content of benzene species was at the expense of a decrease in aliphatic hydrocarbon content [29]. This was due to the aromatization reaction of pyrolysis products and was a process related to olefin cyclization, dehydrogenation, and Diels-Alder reaction enhancement in the gas phase [7,29,30].

Table 3. Weight loss and compound number for pyrolyzed tires at different temperatures

Temperature/ °C	Particle size/mm	>0.850	0.425-0.850	0.250-0.425	0.180-0.250	0.150-0.180	<0.150
200	Types of pyrolytic organic matter	23±2	23±3	21±2	22±1	21±3	34±3
	Weight loss percentages/ wt%	3.47±0.43	3.57±0.18	3.52±0.27	3.51±0.41	3.43±0.37	2.98±0.27
380	Types of pyrolytic organic matter	63±3	70±4	67±3	63±4	80±5	84±4
	Weight loss percentages/ wt%	54.82±1.34	55.21±0.75	57.81±1.34	56.07±0.98	54.43±1.46	39.21±0.96
500	Types of pyrolytic organic matter	28±2	33±4	34±2	31±3	36±4	37±2
	Weight loss percentages/ wt%	67.33±0.85	66.86±1.43	67.62±1.53	67.06±1.43	66.01±1.02	54.6±1.24

Table 4. Tentative GC/MS characterization of waste tire pyrolysis products at 200°C

Particle size/ mm	>0.850	0.425-0.850	0.250-0.425	0.180-0.250	0.150-0.180	<0.150
Compound species (% Area)						
Alcohols	2.56±0.15	2.12±0.37	2.91±0.18		2.66±0.34	1.15±0.14
Nitrogen-containing compound	54.27± 3.15	34.89±1.28	53.15±1.94	47.31±2.04	46.51±2.48	50.67±2.53
Acids	18.11±1.04	37.04±2.46	18.77±1.51	30.39±1.83	28.19±2.15	4.42±0.37
Esters	3.55±0.15	5.99±0.36	3.79±0.11	1.01±0.15	3.2±0.31	29.17±1.54
Alkanes	21.51±1.34	19.71±1.62	21.38±1.57	17.57±1.42	18.04±2.05	14.59±1.61

Table 5. Tentative gc/ms characterization of waste tire pyrolysis products at 380°C

Particle size/ mm	>0.850	0.425-0.850	0.250-0.425	0.180-0.250	0.150-0.180	<0.150
Compound species (% Area)						
Limonene	25.33±1.94	26.14±1.62	23.58±1.64	27.73±0.95	23.2±1.05	22.5±0.73
Olefins	47.88±2.04	43.88±1.27	45.71±2.37	42.2±1.24	34.2±0.67	37.82±1.27
Benzene	3.42±0.16	4.14±0.34	4.84±0.28	4.69±0.19	5.05±0.37	5.22±0.61
Alcohols	12.22±0.84	9.28±0.61	12.72±0.42	8.47±0.37	17.6±0.66	4.81±0.27
Acids	4.13±0.24	6.44±0.38	2.83±0.13	3.89±0.25	5.69±0.73	1.76±0.61
Esters	0.13±0.06		1.02±0.08	1.59±0.16	0.28±0.04	1.21±0.31
Alkanes	2.91±0.42	2.64±0.16	2.47±0.15	0.83±0.36	2.51±0.41	2.45±0.17
Ketones	0.8±0.16	1.48±0.27	1.03±0.07	0.6±0.11	3.73±0.27	2.61±0.34
Halogen-containing substance	3.33±0.95	3.24±0.69	4.54±1.06	3.76±0.55	3.24±0.26	1.69±0.13

Table 6. Tentative gc/ms characterization of waste tire pyrolysis products at 500°C

Particle size/ mm	>0.850	0.425-0.850	0.250-0.425	0.180-0.250	0.150-0.180	<0.150
Compound species (% Area)						
Olefins	10.06±0.55	5.77±0.48	10.45±0.39	10.98±0.64	11.43±1.06	11.43±0.64
Benzene	22.36±0.72	28.3±1.03	19.71±1.26	9.88±0.59	5.82±0.42	0.55±0.15
Alcohol	46.73±1.35	43.75±1.27	44.09±2.15	38.44±1.33	35.93±2.13	15.55±1.85
Alkane	19.62±0.73	20.86±1.02	16.38±1.35	28.8±1.14	9.37±0.45	7.91±0.54
Halogen-containing substance	1.74±0.11	1.59±0.34		4.1±0.68	0.81±0.11	
Sulfur-containing substance	6.05±0.53	2.27±0.26	1.49±0.18	2.9±0.26	24.48±2.15	41.04±2.58

3.4 Effect of tire particle size on pyrolysis products

It is well known that the particle size of input raw materials has a significant effect on the pyrolysis performance by affecting the internal temperature distribution, heating rate and volatilization residence time [11]. In the experiments, the effect of particle size on the composition of pyrolysis products was studied at the pyrolysis temperatures of 200°C, 380°C and 500°C.

As shown in Table 4, when the particle size was less than 0.150 mm, and the temperature was set to 200°C, esters obviously increased from 3.20% to 29.17%. The main ester compounds included bis(2-methylpropyl) phthalate, oxalic acid bis(2-ethylhexyl) ester, 2-ethyl octadecyl oxalate, and phthalate-2-ethylhexyl-ester (Table 7). Since the small particle size provides a larger specific surface area, the plasticizer involved in the decomposition reaction increased. The most commonly used plasticizer was dibutyl phthalate [17,31]. Approximate analysis shows that tire particles with a particle size of less than 0.150 mm contain more inorganic components.

As shown in Table 5, when the temperature was 380°C, with decreases in particle size, the content of benzene derivatives increased slightly, but the content of olefins in contrast. In the thermochemical process, small particles exhibit isothermal behavior and were not limited by internal temperature transfer, which could improve the devolatilization rate of pyrolysis products [15]. The decrease of particle size was conducive to the carbon chain fracture, epoxidation and aromatization of olefins [7]. Primary and secondary reactions can coexist at the same temperature [11]. But in this pyrolysis stage, primary reactions of the tire were dominant, and the aromatization reaction was not violent. When the particle size ranged between 0.180-0.250 mm, more limonene (27.73%) was produced, as can be seen in Table 5. At larger particle sizes, the pyrolysis products cannot be separated from the inside of the particles in time to be further cracked, resulting in a reduction in the content of limonene. It was worth noting that the content of olefins did not show a consistent decrease with the decrease of particle size, and the content of alcohols also shows a fluctuating change. This may be due to the following fact that when the cross-linked structure of the tire was broken under the action of external mechanical force, the structure of the organic matter contained in the tire particles of different particle sizes was different, so the content of the pyrolysis product components presented a fluctuating change.

When the pyrolysis temperature was set to 500°C, and the particle size was less than 0.180 mm, the sulfide componential content increased significantly to 24.48% (Table 6). Table 8 displays that the main compound was cyclohexyl methyl pentadecyl sulfite. According to the molecular formula of cyclohexyl methyl pentadecyl sulfite, it is presumed that the increase may be caused by the combination of cyclohexane (monocyclic benzene generated through addition reaction) and sulfur-containing free radicals. When the particle size was less than 0.180 mm, the content of monocyclic benzene species in the pyrolysis product was reduced. Wang et al. [32] found that high pyrolysis temperature would promote the transfer of sulfur to volatile matter. When the particle size was less than 180 mm, it may have a beneficial effect on the transfer of sulfur to volatile matter.

Table 7. Tentative GC/MS characterization of esters in waste tire pyrolysis products at 200°C

Particle size/ mm Ester species (% Area)	>0.850	0.425-0.850	0.250-0.425	0.180-0.250	0.150-0.180	<0.150
Methyl hexadecanoate	0.92±0.11	0.84±0.13	1.14±0.14	1.01±0.12	1.02±0.26	1.88±0.31
Ethyl hexadecanoate	0.65±0.08		0.79±0.11			0.44±0.08
Methyl octadecanoate	0.56±0.10		0.79±0.15			
Nonyl acetate	1.04±0.21	1.06±0.16	1.07±0.32			
Oxalic acid, bis(2-ethylhexyl) ester	0.38±0.05				1.45±0.25	6.22±0.52
1,2 phthalic acid, (2, ethylhexyl) ester	0.38±0.07	0.3±0.03		0.41±0.08	0.48±0.13	2.19±0.26
Carbonic acid, octadecyl phenyl ester		3.79±0.62				
1,2-phthalic acid, bis(2-methylpropyl) ester						7.77±0.61
Dibutyl phthalate						1.13±0.24
Isopropyl palmitate						0.44±0.08
9,12-octadecadienoic acid, methyl ester						0.31±0.06
2-Acrylic acid, 3-(4-methoxyphenyl)-, 2-ethylhexyl ester						1.66±0.12
Caproic acid, 2-ethyl 1,2-oxalyl bis(oxy-2,1-oxalyl) ester						1.26±0.31
Oxalic acid, 2-ethyl octadecyl ester						3.7±0.27

Table 8. Tentative GC/MS characterization of pyrolysis of benzene series and sulfur-containing substance in waste tire pyrolysis products at 500°C

Particle size/ mm Benzene series and Sulfur-containing substance (% Area)	>0.850	0.425-0.850	0.250-0.425	0.180-0.250	0.150-0.180	<0.150
P-xylene	2.62±0.26	2.31±0.15				
1-ethyl-3-methyl-Benzene	1.82±0.19	2.27±0.22	2.02±0.43			
2-ethyl-1,4-dimethyl-Benzene	0.74±0.11					
(2-methyl-1-propenyl)-Benzene	0.97±0.14	2.4±0.16	2.07±0.37	1.44±0.26	0.9±0.17	
Benzothiazole	6.05±0.62	2.27±0.14				
1,3-dimethyl-1H-Indene	1.46±0.35	1.86±0.21	1.52±0.33	1.32±0.22	0.26±0.08	
1,2,3-Trimethylindole	1.5±0.08					
2,6-dimethyl-Naphthalene	0.85±0.12	1.32±0.15	0.97±0.16	1±0.27	0.55±0.14	
2,4-dimethyl-Quinoline	0.84±0.08			1.15±0.28		
2,3,6-trimethyl-Naphthalene	2.18±0.26	1.12±0.17	0.82±0.24	0.93±0.14	0.64±0.16	
3-(2-Methyl-propenyl)-1H-indole	0.44±0.10					
Diphenylamine	0.69±0.05	0.81±0.21	0.85±0.15	1.76±0.26	0.37±0.11	0.14±0.06
(4,5,5-trimethyl-1,3-cyclopentadien-1-yl)-Benzene	0.36±0.03					
1,2,3,4-tetramethyl-Naphthalene	1.12±0.21	1.43±0.17				
N-phenyl-1,4-Benzenediamine	0.72±0.22	0.89±0.13	0.73±0.13	1.21±0.21		
Aniline		1.99±0.25				
1,3,5-trimethyl-Benzene		4.1±0.24			1.1±0.13	
1-ethyl-2,4-dimethyl-Benzene		0.46±0.15			0.23±0.06	
3-ethenyl-1,2-dimethyl-1,4-Cyclohexadiene		0.71±0.22	0.76±0.22			
2,3-dihydro-4,7-dimethyl-1H-indole		0.93±0.14				
1-methyl-Naphthalene		0.81±0.18	0.66±0.08	0.65±0.15		
2,3-dihydro-1,6-dimethyl-1H-indole		0.35±0.08				

(3-methyl-2-butenyl) Benzene		1.46±0.22				
1,3-dimethyl-1H-indole		0.81±0.06				
(ethoxymethyl)-Benzene			3.61±0.64			
M-xylene			1.78±0.27			
[1-(1,1-dimethylethyl)-3,3-dimethylbutyl]-Benzene			0.58±0.18			
1-methyl-3-(1-methylethyl)-Benzene			0.43±0.09			
1-ethyl-2,3-dihydro-1-methyl-1H-Indene			1.33±0.07			
2,3-dihydro-1,1,5-trimethyl-1H-Indene			0.45±0.11			
1,1,3-trimethyl-1H-Indene			1.13±0.24		0.53±0.14	
p-tert-butyl-Phenol						0.21±0.03
2-(1,1-dimethylethyl)-3-methyl-Phenol						0.2±0.07
1-[1-(S)-(dimethylamino)ethyl]-Naphthalene				2.27±0.26	1.49±0.24	
dl-Erythro-1-phenyl-1,2-propanediol				2.27±0.35	1.49±0.37	
1-Methyl-1,2,3,4-tetrahydronaphthalen-1-ol					0.56±0.13	
2-(1,1-dimethylethyl)-5-methyl-Phenol					0.29±0.08	
Cyclohexyl methyl pentadecyl sulfite.			1.49±0.26	2.9±0.61	23.98±2.31	40.38±2.58
bis(1,1,3,3-tetramethylbutyl) Disulfide					0.5±0.06	0.15±0.05
Sulfurous acid di(cyclohexylmethyl) ester						0.51±0.13

3.5 The formation mechanism of limonene

Limonene was only found in pyrolysis products at the pyrolysis temperature of 380°C (Table 4, Table 5 and Table 6). Chen et al. [16] obtained three exothermic peaks and two endothermic peaks from the DTA thermogram of cis-1,4-polyisoprene at 370°C, 462°C, 544°C and 310°C, 408°C, which explained cis-1,4-polyisoprene basically does not decompose reaction under pyrolysis temperature lower than 310°C, the pyrolysis product cracking caused the limonene content to decrease at pyrolysis temperature higher than 408°C. This confirmed that limonene cannot be detected at 200°C and 500°C pyrolysis products. Pakdel et al. [33] proposed that limonene is the main initial product of rubber pyrolysis. Because the chemical properties of limonene were unstable, decomposition reactions are prone at high temperatures [17]. There are three ways to produce limonene: (1) dimerization of isoprene could generate limonene [34]. Groves et al. [35] assumed that the monomer/dimer ratio increases with increasing temperature and decreases with increasing particle size. Although this path cannot be completely ruled out, the lack of isoprene dimer as a pyrolysis product indicates that this reaction seems impossible to occur in this experiment; (2) The depolymerization of polyisoprene to form a C10 dimer. The activation of this double radical is generated in an oxygen-deficient environment, so it could undergo a cyclization reaction [36, 37]. This dimer was a short-live radical, which could be driven to limonene by two steps of pyrolysis isomerization. The reaction mechanism is shown in Figure 2. However, this mechanism has not been confirmed by specific experimental data, nor does it specify how polyisoprene forms C10 dimers. There was no obvious data to prove the existence of C10 in this reported experiment; (3) The cleavage of the β -bond between the double bonds in the polydipentadiene chain, and the separated propylene group is internally cyclized to form limonene [30,31]. The bond energy of C-C is lower than C=C (347.3 kJ/mol, 611 kJ mol⁻¹ respectively) [38], thus in cis-1,4-polyisoprene, the probability of C-C bond break is greater than that of C=C bond. Due to the difference in bond strength, β -bond breakage was the most favorable in terms of energy [39]. In the study, the explanation for the formation path of limonene was more inclined to the last one. Figure 3 shows that fracture of the β bond in cis-1,4-polyisoprene results in two different allylic radicals, with the radical either two carbons (radical 1) or one carbon (radical 2) separated from the methylated carbon. Under pyrolysis conditions, both of these free radicals could complete the depropagation reaction to obtain the monomer isoprene,

as shown in Figure 4. Radical 1 would undergo intramolecular cyclization, and then break to generate limonene [40]. The intramolecular cyclization of radical 1 to limonene was presented in Figure 5. The fact was that the cleavage of the β bond of the polyisoprene main chain was considered to be more random, radical 1 could continuously reproduce radicals and generate more limonene through the cyclization reaction in Figure 4.

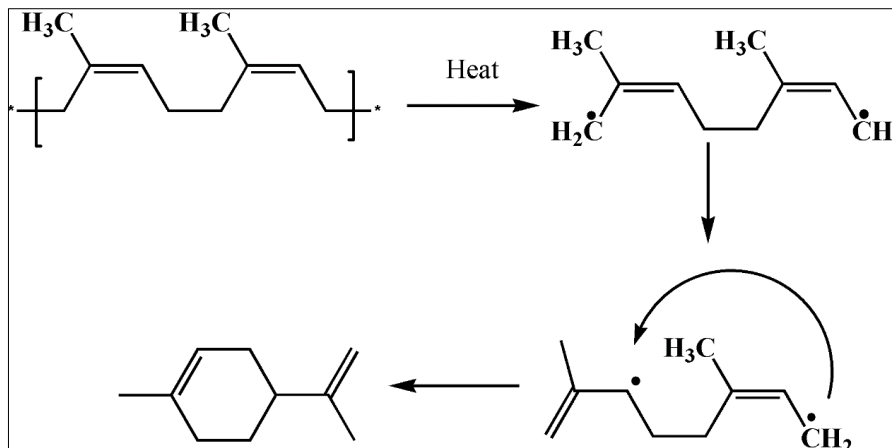


Figure 2. Polyisoprene generates a dimer (C10) free radical, which is then driven to generate limonene by two-step pyrolysis

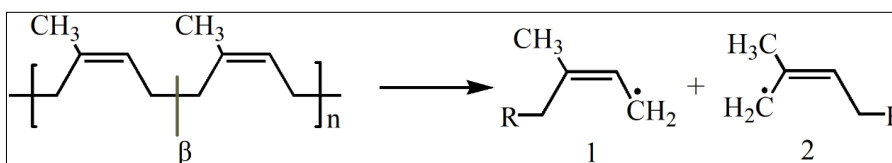


Figure 3. Radical generating depolymerization initiation by scission of the β bond with respect to the double bonds in cis-1,4-polyisoprene

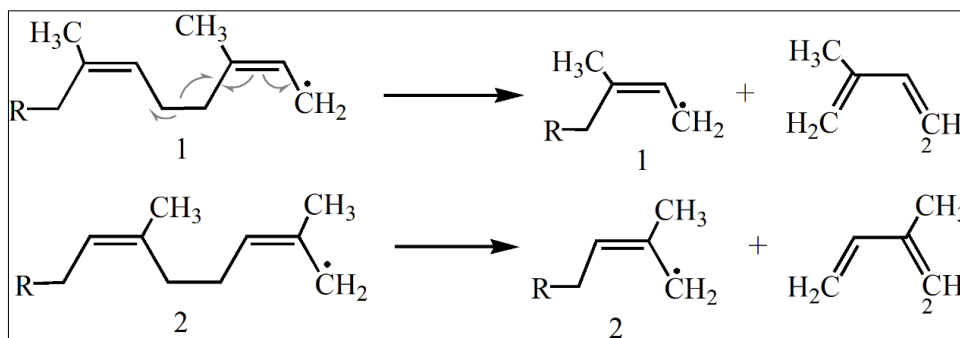


Figure 4. Free radicals 1 and 2 depropagation or decompress to isoprene

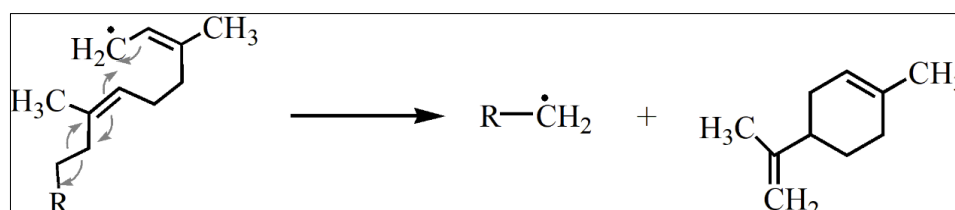


Figure 5. Intramolecular cyclization and scission of allylic radical to form limonene

4. Conclusions

In the experiment reported, the pyrolysis of waste tires was carried out at a pyrolysis temperature of 200°C, 380°C and 500°C. The waste tire particle sizes, which ranged at >0.850mm, 0.425-0.850mm, 0.250-0.425mm, 0.180-0.250 mm, 0.150-0.180mm and <0.150mm was used as the raw material of the pyrolysis process. The results show that the reduction of carbon content will decrease the weight loss rate and the decomposition rate of tires. The pyrolysis behavior of waste tires (all particle sizes) could be divided into three stages: the initial pyrolysis temperature (100-300°C), maximum weight loss pyrolysis temperature (300-500°C), and the final pyrolysis temperature (500-680°C). The aromatization reaction of olefins led to an increase in the content of benzene species with the temperature increased. When the pyrolysis temperature was the same, the fewer the particle sizes, the more product types were formed. At the pyrolysis temperature of 380°C, as the particle size decreases, the limonene content first increases and then decreases. The content of limonene reached the maximum value of 27.73% when the particles were 0.180-0.250mm. The sulfur content increased significantly when the pyrolysis temperature was 500°C and the particle sizes were less than 0.180mm. The irregular change of the composition of pyrolysis products may also be related to the different structures of organic matter in particle size. The formation pathway of limonene may be the cleavage of the β -bond between the double bonds in cis-1,4-polyisoprene to generate free radicals, which undergo intramolecular cyclization. The results of the experiments show that the content of target products such as limonene can be increased by controlling the pyrolysis temperature and the particle size of the raw input materials, while also reducing the content of sulfur-containing substances. The goal of increasing the value of reported tire pyrolysis products has been achieved by the investigation.

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