Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.jzus.zju.edu.cn; www.springerlink.com
E-mail: jzus@zju.edu.cn

Effective and green tire recycling through microwave pyrolysis

Yu-zhe ZHANG[1], Ting-ting BIAN[1], Yi ZHANG[1], Xu-dong ZHENG[1], Zhong-yu LI[†‡1,2,3]

[1]*School of Environmental and Safety Engineering, Changzhou University, Changzhou 213164, China*
[2]*Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China*
[3]*Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Changzhou University, Changzhou 213164, China*
[†]E-mail: zhongyuli@mail.tsinghua.edu.cn

Received July 1, 2018; Revision accepted Sept. 14, 2018; Crosschecked Nov. 14, 2018

Abstract: Waste tire rubber has become a severe environmental issue, which calls for a green method to recycle this rubber. Microwave thermolysis serves as an ideal recycling process for used tires. By surveying the dielectric characteristics from 25 to 700 °C under microwave frequencies of 915 and 2466 MHz, the microwave absorption ability of waste tire rubbers was studied. At temperatures below 350 °C, the dielectric characteristics were relatively steady. Both the loss factor and relative dielectric constant (DC) increased sharply with the rise in temperature. The reason for this is the release of volatile substances, which increases the electrical conductivity. The performance of microwave absorption of tire rubber during thermolysis, and thus the efficiency of microwave tire rubber thermolysis, can be largely impacted by the specimen dimension. The calculation of the reflection loss (RL) of the tire rubber specimens suggests that when the waste tire rubber is 5 mm thick, the highest microwave absorption can be achieved at 915 MHz and 592.1 °C, with RL of −17.30 dB. The product after microwave pyrolysis of waste tire rubber comprises 35% carbon black, 40% oil, and 25% gas. Based on this investigation of the optimal condition of microwave absorption, a proper microwave pyrolysis recycling system was designed for waste tire. This system is efficient at recycling the waste tire rubber into valuable carbon black, oil, and gas products.

Key words: Recycling system; Waste tires; Microwave; Thermolysis; Carbon black; Oil; Gas
https://doi.org/10.1631/jzus.A1800388 **CLC number:** X734.2

1 Introduction

Waste tires have become a serious economic and environmental issue, as they are difficult to dispose of and recycle. The development of an efficient disposal and recycling method of the waste tires is in high demand. Currently, landfill disposal is the most frequently used disposal method for waste tires. Yet, various degradation methods, for instance, chemical and biological degradation, are ineffective on waste tires. Landfill waste tires occupy valuable ground for an extenden period. Besides, waste tires lead to many health issues via trapped rainwater, which allows stagnant bodies of water to breed insects that carry diseases, and pose fire hazards. Other chemical or mechanical methods for recycling waste tires include incineration, which generates energy through waste tire combustion. Yet, these methods also result in SO_2, NO_x, and other toxic gases that should be treated being emitted.

The focus of this study is the pyrolysis method, which is a potential way for recycling valuable contents from used tires. Waste tires can be pyrolyzed in a variety of ways, e.g. in rotary kilns. The thermolysis process of rotary kilns is an indirect heating method that consumes considerable energy. It is also an inefficient solution owing to the imbalance heat transfer through the kiln wall. In addition, this process needs

---

[‡] Corresponding author

ORCID: Zhong-yu LI, https://orcid.org/0000-0001-8086-7461 air for heating transmission. Owing to the reaction between waste tires and air at high temperature, rotary kiln thermolysis of waste tires yields numerous toxic products.

Accordingly, microwave thermolysis is the major recycling method chosen for this study. Microwave heating has several advantages. Because the material is capable of absorbing microwave at the molecular level, this direct heating method is obviously more efficient than other methods are. It also stops and restarts rapidly. Furthermore, as the air is replaced with N_2 in the recycling system, few toxic products are generated during the thermolysis process. Other advantages of microwave processing include selective heating for materials, a higher level of automation and safety, as well as less process time and lower energy consumption.

In recent years, the pyrolysis technique of waste tires has piqued the attention of scientists and technicians worldwide. Though the effects of temperature (Casal et al., 2005; Jia et al., 2009; Shuang et al., 2010), granule magnitude (Lee et al., 1995; Zhu et al., 2008; Sadhukhan et al., 2011), and calefaction method on thermolysis as well as its product compositions have been studied widely (Dai et al., 2001; Mui et al., 2004; Kato et al., 2011), the microwave absorption ability of waste tire rubber rarely has been studied. As microwave technology has been progressively applied in scientific research and industrial production (Peng et al., 2012), it is critical to study the microwave absorption capability of waste tires (Lee et al., 1995; Metaxas, 2000; Peng et al., 2010, 2012; Gupta et al., 2011a).

It is generally known that the microwave absorbing properties of waste tires are associated with the dielectric properties of the tires. Some scholars (Lee et al., 1995; Ariyadejwanich et al., 2003; Huang and Tang, 2009; Gupta et al., 2011b) have tried to characterize the dielectric properties of waste tires. The results suggest that the organic compounds of rubber have a low dielectric loss (DL) and are almost transparent to microwave at 25 °C.

Components with a high DL in waste tires, e.g. some metal elements, may improve the microwave absorption ability of tire rubber (Peng et al., 2010). It is reported that the microwave absorption of waste tires is significantly affected by the heating temperature (Al-Harahsheh and Kingman, 2004; Bignozzi and Sandrolini, 2006; Sun, 2006; Peng et al., 2011). Yet, only a narrow range of temperature in the pyrolysis of waste tires, generally less than 200 °C, has been studied; hence, a more detailed study of microwave absorption by waste tires over a wide temperature range should be conducted (Levendis et al., 1996; Bartoli et al., 2018; Fang et al., 2018; Nisar et al., 2018; Zeaiter et al., 2018). The aims of the present study were to pyrolyze tire rubber using a microwave method under a reaction temperature range of 25–700 °C (Caponero et al., 2003, 2004, 2005; Khani et al., 2010; Mittal et al., 2010; Ahmaruzzaman and Gupta, 2011; Gupta et al., 2011b, 2013; Saleh and Gupta, 2012a, 2014; Saravanan et al., 2016) and analyze the optimum conditions for the tire pyrolysis as well as the properties of the products.

Through our research, the following contributions were made:

1. Recycling efficiency metrics: Three measurements are correlated with the efficiency of waste tires recycling (Zhou et al., 2006; Gupta and Saleh, 2013; Saravanan et al., 2013a; Devaraj et al., 2016). (1) Conductivity measurement: models the relationship between the efficiency and temperature (Mohammadi et al., 2011; Saleh and Gupta, 2011, 2012b; Karthikeyan et al., 2012; Saravanan et al., 2013b); (2) Penetration depth: yields the math correlation between frequency and absorbing efficiency (Ghaedi et al., 2015; Saravanan et al., 2015a, 2015b; Robati et al., 2016); (3) Reflection loss (RL): takes the sample thickness into account and serves as our final measure of the recycling efficiency.

2. Optimal condition for recycling (Saravanan et al., 2013c, 2013d; Gupta et al., 2014, 2015; Asfaram et al., 2015; Rajendran et al., 2016): Using the three metrics mentioned above, we performed several experiments and investigated the optimal conditions of the recycling system with respect to ambient temperature, microwave frequency, and sample thickness. It was found that the system can achieve the best efficiency at 915 MHz and 592.1 °C with 5 mm thick waste tire rubber.

3. Recycling system: The optimal properties listed above were employed to build an efficient recycling system for waste tires through microwave pyrolysis.

2 Experimental

2.1 Investigation on the optimal condition for recycling the waste tires

2.1.1 Preparation of tire sample

The waste tire samples for the experiments were provided by the Cooper Company, Michigan, USA.

For the dielectric properties measurement, the tire samples were restricted to a diameter of (3.60±0.15) mm and a length of (13.59±0.05) mm regarding particle size and the mass of the samples with (0.153±0.002) g. The major component of the samples used in the experiments was rubber. All the experiments in this study were performed under the TM_{0n0} cavity system.

2.1.2 Key measurement for the waste tire recycling

Before the experimental results are described, the metric of evaluation, i.e. the recycling efficiency, is introduced in this section. One of the most significant metrics of the recycling efficiency is the efficiency of microwave absorption. The first measurement is the dielectric response of a material. For nonmagnetic dielectrics, the formulation of the response is associated with the permittivity (ε), because of the dielectric response of a material in accordance with the temperature range and frequency. The permittivity (ε) can be formulated as (Metaxas, 2000; Mui et al., 2004; Kato et al., 2011)

$$\varepsilon=\varepsilon_0\varepsilon_r=\varepsilon_0(\varepsilon_r' - \mathrm{j}\varepsilon_r''), \quad (1)$$

where $\varepsilon_0=8.8854\times10^{-12}$ F/m is a constant denoting the permittivity of free space. j is an imaginary unit of a complex number and $\mathrm{j}^2=-1$. ε_r is the complex dielectric constant (DC), used to describe the constitutive connection between the electric flux density and electric field intensity in loss dielectrics. Because ε_r is a complex number, it can be decomposed into two parts: the imaginary portion ε_r'' and the real portion ε_r'. The imaginary portion ε_r'' is the relative DL factor and the real part ε_r' is the relative DC. Based on the relevant studies, the imaginary part is the metric of the loss of electrical energy in dielectrics (Metaxas, 2000; Mui et al., 2004; Kato et al., 2011). The real one measures the dielectric's ability to store electrical energy. The energy difference from the electric one to the dielectric area is transformed into thermal or heat energy. Then the imaginary number of ε_r is the heating rate of the microwave energy to dielectrics with no magnetic response.

Assuming that the free electron conductivity is the major cause of DL, and the final-state DL measurement is approximately the directly heated sample resistance at ambient temperature.

2.1.3 Conductivity measurement

It is assumed that the free electron conductivity is primarily attributed to the DL. The mathematical relationship (Peng et al., 2012) between the DC resistance and the DL factor is defined as

$$\varepsilon_r''=\frac{1}{2\pi f\varepsilon_0 R[\pi D^2/(4L)]}, \quad (2)$$

where f is the frequency of microwave, D is the diameter of the sample, L is the sample length, and R is the resistance measured in the experiments. To calculate a theoretical DL factor, the value of DC resistance should be used. Then, the DL factor is compared with the measured DL factor to test the microwave loss mechanism. By Eq. (2), it was concluded that the recycling efficiency of the waste tires is associated with the frequency of the microwave and the ambient temperature.

2.1.4 Penetration depth calculation

In the present study, the technique of cavity perturbation was employed to measure the dielectric properties (ε_r', ε_r'') of the rubber during the thermolysis at the microwave frequencies of 915 and 2466 MHz. The cavity perturbation technique is used to measure the differences in the form of frequency changes and in quality factors. Such differences result from the microwave cavity containing a sample holder with the same sample in an empty specimen holder (Peng et al., 2010). Thus, the DC calculation is necessary to assess such changes.

As mentioned above, the efficiency of recycling the waste tires is correlated with the microwave absorption ability of the tires. Accordingly, the penetration depth D_p, which is the parameter used to evaluate a material's microwave absorption ability, should be introduced. It is equal to the distance from the surface into a material for which the wave power drops to 1/e from its original value on the surface (Peng et al., 2010), where e refers to the base number of natural logarithms. The penetration depth can be calculated from the DL factor and relative DC by the following equation (Peng et al., 2012):

$$D_{\mathrm{p}}=\frac{\lambda_0}{2\pi(2\varepsilon_{\mathrm{r}}')^{1/2}}\left\{\left[1+\left(\frac{\varepsilon_{\mathrm{r}}''}{\varepsilon_{\mathrm{r}}'}\right)^2\right]^{1/2}-1\right\}^{-1/2}, \qquad (3)$$

where λ_0 denotes the wavelength of the microwave in free space.

2.1.5 Reflection loss calculation

The RL calculation also serves as a measurable metric. Because microwave heating is conducted in a metallic cavity, the RL is used to study the microwave absorption ability of a sample. The calculation of RL (Peng et al., 2012) is shown as

$$\mathrm{RL}=20\log\frac{\left|\sqrt{\frac{\mu_{\mathrm{r}}}{\varepsilon_{\mathrm{r}}}}\tanh\left(\mathrm{j}\frac{2\pi f}{c}\sqrt{\mu_{\mathrm{r}}\varepsilon_{\mathrm{r}}}d\right)-1\right|}{\left|\sqrt{\frac{\mu_{\mathrm{r}}}{\varepsilon_{\mathrm{r}}}}\tanh\left(\mathrm{j}\frac{2\pi f}{c}\sqrt{\mu_{\mathrm{r}}\varepsilon_{\mathrm{r}}}d\right)+1\right|}, \qquad (4)$$

where μ_{r} denotes the complex relative permeability of a sample, which is assumed to be 1 in the calculation of the RL of waste tire, d is the sample thickness, and c is the velocity of microwaves in free space. In the following section, the two measurements RL and D_{P} are used to seek out the optimal condition of waste tire recycling.

2.2 Microwave-based waste tires recycling system

The microwave pyrolysis system consists of a microwave oven, condenser, oil-gas separator, oil chamber, gas collecting bag, and air inlet (Fig. 1). Before being delivered to the microwave pyrolysis system, the tire is cut into pieces with a diameter of (3.60±0.15) mm, a length of (13.59±0.05) mm, and a thickness of (5±0.03) mm. Nitrogen is added into the system via the air inlet, so that the air can be removed from the system. Then, using the microwave oven control system, the temperature in the oven was increased to 592.1 °C and then kept constant. The time required for microwave thermolysis is usually 20–30 min, depending on the thermolysis conditions. The high temperature gases produced during the rubber thermolysis are led into the condenser via the gas pipeline. The combustible gases that can not be condensed are mixed with the oil that flows into the oil-gas separator via pipeline. The oil will flow into the oil chamber and the gas will move to the reservoir bag. The only solid product is carbon black, which can be removed from the microwave oven after the pyrolysis.

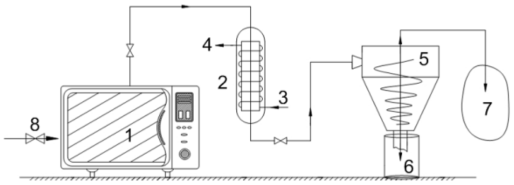


Fig. 1 Diagram of the microwave pyrolysis system for tire
1: microwave oven; 2: condenser; 3: inflow condensation water; 4: outflow condensation water; 5: oil-gas separator; 6: oil chamber; 7: reservoir bag; 8: air inlet, which replacing the air with N_2

3 Results and discussion

3.1 Optimal conditions

Excessive temperature in the heating process causes the tire to pyrolyze before it receives the microwave, which affects the quality of the used tires involved in the experiment and further affects the quality of the final product.

Temperature versus the dielectric parameters is shown in Fig. 2. Since it is important to calculate the RL and D_{P}, i.e. two important measurements of recycling efficiency, there are four different stages. As the temperature increases to 350 °C, the relative DC value changes little. In the next stage, a sharp increase and decrease corresponding to the relative DC value is observed at temperature ranging from 350 to 450 °C. Next, another substantial increase in the relative DC is observed at temperatures ranging from 450 to 650 °C, as shown in Figs. 2a and 2b. When temperature is above 650 °C, the DC remains unchanged and relatively high. The results of DL factor are as above, as shown in Figs. 2c and 2d. The only difference is that the DL peak corresponds to a temperature of 450 to 650 °C. This normally would suggest a variation in the material under an insulating

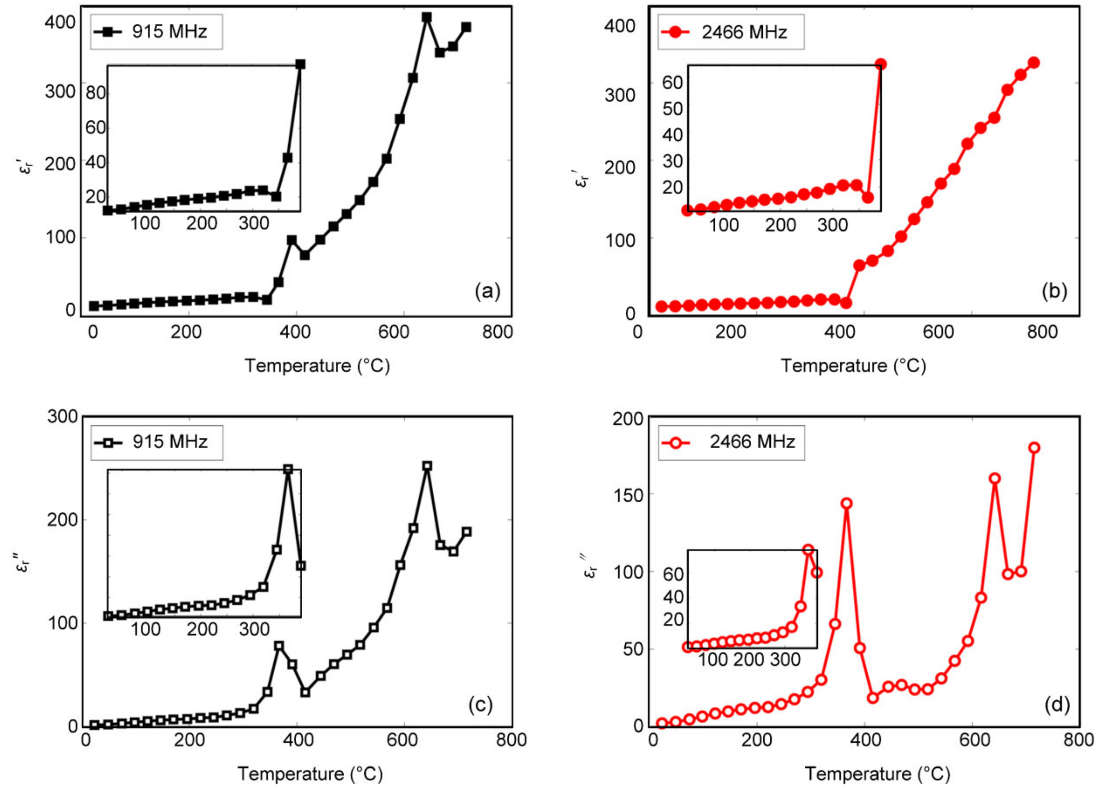


Fig. 2 Temperature dependences of dielectric properties of the waste tire samples. Insets: magnification patterns as temperature varies from 24 to 350 °C

(a) Temperature vs ε_r' at 915 MHz; (b) Temperature vs ε_r' at 2466 MHz; (c) Temperature vs ε_r'' at 915 MHz; (d) Temperature vs ε_r'' at 2466 MHz

barrier loss (Peng et al., 2012). This result may also suggest a main phase transformation occur in the temperature range (Peng et al., 2012).

The value of the relative DC of waste tire is independent of the microwave frequency (Fig. 2). When the temperature is rising, the relative DL factor at 915 MHz is larger than that at 2466 MHz (Fig. 2). This results from the inversely proportional relationship between microwave frequency and the relative DL factor (Eq. (2)). These results suggest that 915 MHz is the better microwave frequency to use in the recycling system.

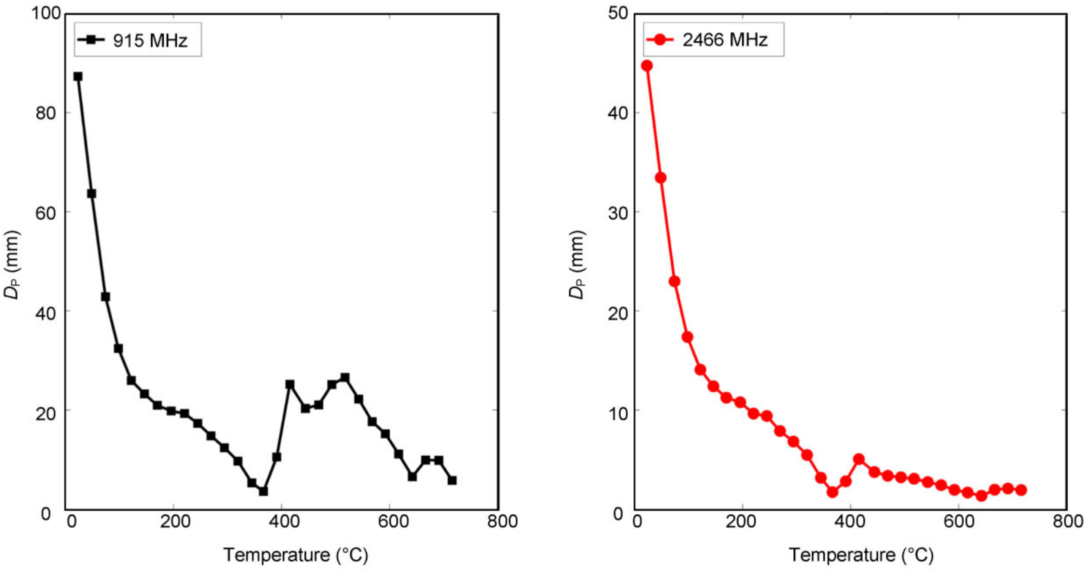
The changes in microwave penetration depth of the tire rubber during the pyrolysis process are shown in Fig. 3. It is important to note that the depth first decreases with the rise in temperature until 380 °C, and then increases shortly as the temperature continues to rise. Then, it decreases again after 450 °C. The middle increase actually results from the metal elements in the middle of the tire sample. The DL factor of the waste tire rubber decreases as the metal elements, including Fe, decrease which leads to a major addition in the microwave penetration depth. For instance, the penetration depths are shown as 15 mm at 915 MHz and 5 mm at 2466 MHz, when the temperature reaches 592.1 °C. The penetration depth at 915 MHz is always larger than that at 2466 MHz at the same temperature. Based on that, the maximum microwave absorption can be achieved when the frequency is 915 MHz. Thus, 915 MHz is the optimal condition for the recycling of waste tires.

The only question left is to determine the optimal sample thickness for recycling the rubber. The RL changes when the temperature increases at 915 MHz with the waste tire sample thickness varying from 5 to 30 mm (Fig. 4). In Fig. 4, there is an absorption peak around 592.1 °C when the thickness of the sample is 5 mm. With the increase in the sample's thickness, this highest point of absorption then moves to a lower temperature area. The different RL curves suggest that the position of absorption peak is associated with the thickness of the sample. In addition, the maximum RL value achieved is −17.30 dB with a thickness of 5 mm. This phenomenon is attributed to the periodicity of microwaves traveling in the medium. The similar RL curve shifts are observed at lower temperatures.

The RL curves at 2466 MHz are also shown in Fig. 5 for comparison. It is also found that the sample with the thickness of 5 mm reaches the peaked microwave absorption with the thickness ranging from 5 to 30 mm. Besides, the pattern of RL curves remains similar to that at 915 MHz. The major difference between the two figures is the value of RL in the peak. The maximum microwave absorption with respect to the RL value is −6.27 dB at 2466 MHz, which is much higher than that at 915 MHz. This is attributed to the differences between the DL factors at 915 and 2466 MHz and that between wavelengths of these two frequencies.

It is found from these results that the tire rubber recycling is also susceptible to the sample thickness. The optimal sample thickness concluded from the experiments is 5 mm under the frequency of 915 MHz.

To summarize the results of this section, a temperature of 592.1 °C, a tire particle thickness of 5 mm, and a microwave frequency of 915 MHz contribute to the tire recycling through microwave pyrolysis.



(a)

(b)

Fig. 3 Temperature dependence of microwave penetration depth of tire at 915 MHz (a) and 2466 MHz (b)

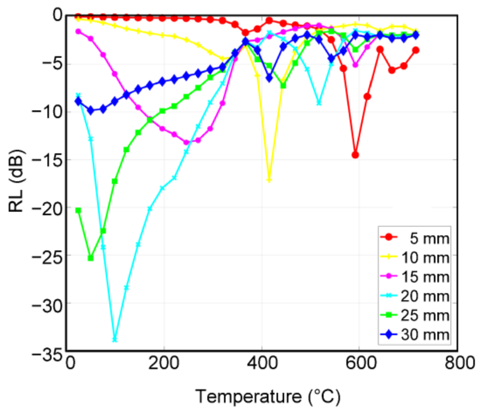


Fig. 4 Reflection loss of tire rubber versus temperature at 915 MHz with different thicknesses

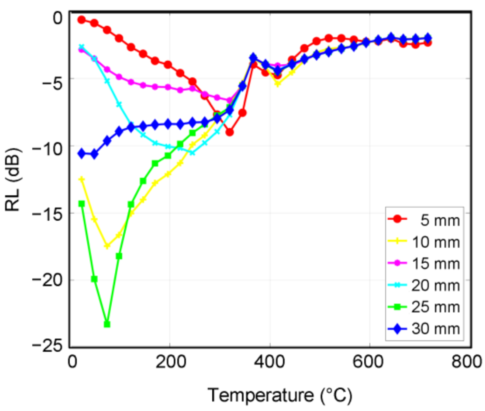


Fig. 5 Reflection loss of tire versus temperature at 2466 MHz with different thicknesses

3.2 Microwave-based waste tires recycling system

By studying myriad experimental data, it is found that the thicknesses of tire particles are about 5 mm and the microwave frequency is 915 MHz when the temperature reaches 592.1 °C. Besides, the waste tires could be completely decomposed at the peaked efficiency. Using the microwave pyrolysis, low value-added waste tires were transformed into various materials, including oils and carbon black. These transformed materials are critical in industrial production and our lives.

The product of the waste tire after microwave pyrolysis comprises 35% carbon black, 40% oil, and 25% gas.

Oils are obtained by condensing of high-temperature gas generated during the tire pyrolysis, and the components are listed in Table 1. The oil is composed of 19.8% aliphatic hydrocarbon, 55.2% aromatic hydrocarbon, 12.6% heteroatom/polar substance and 12.4% asphaltene. The most hydrocarbon with the highest economic value is DL-limonene, which has a specific gravity of 0.421%. It is considered a highly valuable industrial organic solvent, additive and oil resin pigment dispersant. It can also act as a substitute for chlorofluorocarbons in cleaning circuit boards. In addition, considerable *o*-xylene and toluene are present in the aromatic hydrocarbon, the proportions of which are 5.336% and 5.268%, respectively. The former can be applied in the production of phthalic anhydride (*o*-benzoic anhydride, PA), dyestuff, insecticide, etc. The latter is a vital raw material for the organic chemical industry and the most widely used solvent in the pharmaceutical, chemical, and dyestuff industries. As incomplete statistics suggests, the total output of toluene in 2017 was 40 million tons. If the waste tires produced globally each year are decomposed, the yield of toluene will reach 800 thousand tons per year, taking up 2% of the total consumption of toluene worldwide.

In general, a lot of carbon black will be introduced in the manufacture of automobile tires and can be separated through the pyrolysis of tires. For carbon black, the size of the specific surface area serves as the primary index for the classification of carbon black varieties, and the carbon black with a large surface area outperforms others in application of the rubber. The performance of carbon black, which is obtained by pyrolysis of tires, is listed in Table 2. It is found that, the reinforcement performance and quality of pyrolysis carbon black are better than those of commercial carbon black N550. It is suitable for natural rubber and various synthetic rubber products. Owing to its excellent properties, it has excellent commercial application value.

Table 1 Pyrolysis oil components

Component	Content (%)*	Main component	Content (%)*
Aliphatic hydrocarbon	19.8	Pentacosane	1.158
		N-hexacosane	0.923
		1-methyl-4 isopropyl cyclopropane	0.896
		N-heptacosane	0.704
		N-heptadecane	0.452
		DL-limonene	0.421
Aromatic hydrocarbon	55.2	*o*-xylene	5.336
		Methylbenzene	5.268
		Ethylbenzene	2.303
		Trimethylbenzene	2.052
		Trimethyl-naphthalene	1.763
		Benzene	1.532
Heteroatom/ Polar substance	12.6	Hexahydro-2h-azoketone	4.651
		4-Methylquinoline	2.397
		4-Methylbenzyl phenol	0.319
Asphaltene	12.4		

* The percentage of weight

Table 2 Properties of pyrolysis carbon black

Property	Pyrolysis carbon black
Iodine absorption value (g/kg)	167.0
Total surface area ($\times 10^3$ m^2/kg)	63.0
Adsorption ratio surface area ($\times 10^3$ m^2/kg)	59.0
External surface area ($\times 10^3$ m^2/kg)	43.0
Ash content (%)*	10.9

* The percentage of weight

The gas unable to condensate during the pyrolysis of the tire is gathered, and its major components are listed in Table 3. The contents of methane, ethylene, and hydrogen take up nearly 57% of the total gas mass. Generally speaking, the calorific values of methane and hydrogen are 39 829 and 12 789 kJ/m^3, respectively, and the heat value of ethylene is 63 400 kJ/m^3. Thus, these gases contain a huge amount of energy, which can be used in the burning power of the power plant. In addition, the S element content of these gases is very low, which make them an environmentally friendly and clean energy. Recycling waste tires to generate combustible gas can reduce the use of coal, which is of great significance to environmental protection.

Table 3 Components of pyrolysis gas

Component	Content (%)*
Carbon monoxide	3.870
Hydrogen	8.130
Methane	29.360
Hydrogen sulfide	0.102
Ethane	12.680
Ethylene	20.030
Pentane	0.633

* The percentage of molar

In the entire microwave reaction, the waste tire rubber may cause temperature variation during the microwave process, which may have some impacts on the experimental data.

In brief, the recycling of waste tires by microwave pyrolysis not only reduces environmental pressure but also improves the utilization of social resources. As a result, it facilitates the sustainable development of human and ecological environment and is of great significance to all countries worldwide.

4 Conclusions

The optimal conditions of recycling waste tires through microwave pyrolysis were investigated in this study. The measurement of waste tire rubber dielectric properties was performed during thermolysis from 25 to 750 °C under microwave frequencies of 915 and 2466 MHz. Although the dielectric characteristics remained relatively steady at low temperatures, the loss factor and relative DC of waste tire rubber showed a sudden increase above 592.1 °C, which results from the release of volatile matter. During the thermolysis, the devolatilizing of the waste tires resulted in the conductivity rising, indicating that the delocalized electrons density will show an increase. The computation of microwave penetration depth identified that the microwave absorption ability of the tire rubber was considerably improved by the process of thermolysis at high temperatures. The RL computation of the tire rubber specimen proved that the maximum microwave absorption can be achieved when the waste tire thickness is increased to 5 mm at 915 MHz and 592.1 °C, with RL value of −17.30 dB. Based on these conditions, a waste tire recycling system will be designed for the waste tires. It has been shown that this system can efficiently recycle the value contents from waste tires such as carbon black, scrap steel, and oil. The characteristics and component details of these products will be studied in further research.

References

Ahmaruzzaman M, Gupta VK, 2011. Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. *Industrial & Engineering Chemistry Research*, 50(24): 13589-13613.
https://doi.org/10.1021/ie201477c

Al-Harahsheh M, Kingman SW, 2004. Microwave-assisted leaching—a review. *Hydrometallurgy*, 73(3-4):189-203.
https://doi.org/10.1016/j.hydromet.2003.10.006

Ariyadejwanich P, Tanthapanichakoon W, Nakagawa K, et al., 2003. Preparation and characterization of mesoporous activated carbon from waste tires. *Carbon*, 41(1):157-164.
https://doi.org/10.1016/S0008-6223(02)00267-1

Asfaram A, Ghaedi M, Agarwal S, et al., 2015. Removal of basic dye Auramine-O by ZnS:Cu nanoparticles loaded on activated carbon: optimization of parameters using response surface methodology with central composite design. *RSC Advances*, 5(24):18438-18450.
https://doi.org/10.1039/C4RA15637D

Bartoli M, Rosi L, Giovannelli A, et al., 2018. Microwave assisted pyrolysis of crop residues from *Vitis vinifera*. *Journal of Analytical and Applied Pyrolysis*, 130:305-313.
https://doi.org/10.1016/j.jaap.2017.12.018

Bignozzi MC, Sandrolini F, 2006. Tyre rubber waste recycling in self-compacting concrete. *Cement and Concrete Research*, 36(4):735-739.
https://doi.org/10.1016/j.cemconres.2005.12.011

Caponero J, Tenório JAS, Levendis YA, et al., 2003. Emissions of batch combustion of waste tire chips: the afterburner effect. *Energy & Fuels*, 17(1):225-239.
https://doi.org/10.1021/ef0201331

Caponero J, Tenório JAS, Levendis YA, et al., 2004. Emissions of batch combustion of waste tire chips: the hot flue-gas filtering effect. *Energy & Fuels*, 18(1):102-115.
https://doi.org/10.1021/ef030043b

Caponero J, Tenório JAS, Levendis YA, et al., 2005. Emissions of batch combustion of waste tire chips: the pyrolysis effect. *Combustion Science and Technology*, 177(2):347-381.
https://doi.org/10.1080/00102200590900516

Casal MD, Canga CS, Díez MA, et al., 2005. Low-temperature pyrolysis of coals with different coking pressure characteristics. *Journal of Analytical and Applied Pyrolysis*, 74(1-2):96-103.
https://doi.org/10.1016/j.jaap.2004.10.012

Dai XW, Yin XL, Wu CZ, et al., 2001. Pyrolysis of waste tires in a circulating fluidized-bed reactor. *Energy*, 26(4):385-399.
https://doi.org/10.1016/S0360-5442(01)00003-2

Devaraj M, Saravanan R, Deivasigamani R, et al., 2016. Fabrication of novel shape Cu and Cu/Cu_2O nanoparticles modified electrode for the determination of dopamine and paracetamol. *Journal of Molecular Liquids*, 221:930-941. https://doi.org/10.1016/j.molliq.2016.06.028

Fang SW, Gu WL, Dai MQ, et al., 2018. A study on microwave-assisted fast co-pyrolysis of chlorella and tire in the N_2 and CO_2 atmospheres. *Bioresource Technology*, 250:821-827. https://doi.org/10.1016/j.biortech.2017.11.080

Ghaedi M, Hajjati S, Mahmudi Z, et al., 2015. Modeling of competitive ultrasonic assisted removal of the dyes–Methylene blue and Safranin-O using Fe_3O_4 nanoparticles. *Chemical Engineering Journal*, 268:28-37. https://doi.org/10.1016/j.cej.2014.12.090

Gupta VK, Saleh TA, 2013. Sorption of pollutants by porous carbon, carbon nanotubes and fullerene-an overview. *Environmental Science and Pollution Research*, 20(5): 2828-2843. https://doi.org/10.1007/s11356-013-1524-1

Gupta VK, Gupta B, Rastogi A, et al., 2011a. Pesticides removal from waste water by activated carbon prepared from waste rubber tire. *Water Research*, 45(13):4047-4055. https://doi.org/10.1016/j.watres.2011.05.016

Gupta VK, Jain R, Nayak A, et al., 2011b. Removal of the hazardous dye—tartrazine by photodegradation on titanium dioxide surface. *Materials Science and Engineering: C*, 31(5):1062-1067. https://doi.org/10.1016/j.msec.2011.03.006

Gupta VK, Kumar R, Nayak A, et al., 2013. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *Advances in Colloid and Interface Science*, 193-194:24-34. https://doi.org/10.1016/j.cis.2013.03.003

Gupta VK, Nayak A, Agarwal S, et al., 2014. Potential of activated carbon from waste rubber tire for the adsorption of phenolics: effect of pre-treatment conditions. *Journal of Colloid and Interface Science*, 417:420-430. https://doi.org/10.1016/j.jcis.2013.11.067

Gupta VK, Nayak A, Agarwal S, 2015. Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environmental Engineering Research*, 20(1):1-18. https://doi.org/10.4491/eer.2015.018

Huang H, Tang L, 2009. Pyrolysis treatment of waste tire powder in a capacitively coupled RF plasma reactor. *Energy Conversion and Management*, 50(3):611-617. https://doi.org/10.1016/j.enconman.2008.10.023

Jia Q, Che DF, Liu YH, et al., 2009. Effect of the cooling and reheating during coal pyrolysis on the conversion from char-N to NO/N_2O. *Fuel Processing Technology*, 90(1): 8-15. https://doi.org/10.1016/j.fuproc.2008.07.010

Karthikeyan S, Gupta VK, Boopathy R, et al., 2012. A new approach for the degradation of high concentration of aromatic amine by heterocatalytic Fenton oxidation: kinetic and spectroscopic studies. *Journal of Molecular Liquids*, 173:153-163. https://doi.org/10.1016/j.molliq.2012.06.022

Kato T, Yoshikawa N, Taniguchi S, et al., 2011. Microwave magnetic field heating of a cobalt-based amorphous ribbon. *Japanese Journal of Applied Physics*, 50(3R):033001. https://doi.org/10.1143/JJAP.50.033001

Khani H, Rofouei MK, Arab P, et al., 2010. Multi-walled carbon nanotubes-ionic liquid-carbon paste electrode as a super selectivity sensor: application to potentiometric monitoring of mercury ion(II). *Journal of Hazardous Materials*, 183(1-3):402-409. https://doi.org/10.1016/j.jhazmat.2010.07.039

Lee JM, Lee JS, Kim JR, et al., 1995. Pyrolysis of waste tires with partial oxidation in a fluidized-bed reactor. *Energy*, 20(10):969-976. https://doi.org/10.1016/0360-5442(95)00049-M

Levendis YA, Atal A, Carlson J, et al., 1996. Comparative study on the combustion and emissions of waste tire crumb and pulverized coal. *Environmental Science & Technology*, 30(9):2742-2754. https://doi.org/10.1021/es950910u

Metaxas R, 2000. Radio frequency and microwave heating: a perspective for the millennium. *Power Engineering Journal*, 14(2):51-60. https://doi.org/10.1049/pe:20000206

Mittal A, Mittal J, Malviya A, et al., 2010. Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *Journal of Colloid and Interface Science*, 344(2):497-507. https://doi.org/10.1016/j.jcis.2010.01.007

Mohammadi N, Khani H, Gupta VK, et al., 2011. Adsorption process of methyl orange dye onto mesoporous carbon material–kinetic and thermodynamic studies. *Journal of Colloid and Interface Science*, 362(2):457-462. https://doi.org/10.1016/j.jcis.2011.06.067

Mui ELK, Ko DCK, McKay G, 2004. Production of active carbons from waste tyres—a review. *Carbon*, 42(14): 2789-2805. https://doi.org/10.1016/j.carbon.2004.06.023

Nisar J, Ali G, Ullah N, et al., 2018. Pyrolysis of waste tire rubber: influence of temperature on pyrolysates yield. *Journal of Environmental Chemical Engineering*, 6(2): 3469-3473. https://doi.org/10.1016/j.jece.2018.05.021

Peng ZW, Hwang JY, Mouris J, et al., 2010. Microwave penetration depth in materials with non-zero magnetic susceptibility. *ISIJ International*, 50(11):1590-1596. https://doi.org/10.2355/isijinternational.50.1590

Peng ZW, Hwang JY, Mouris J, et al., 2011. Microwave absorption characteristics of conventionally heated non-stoichiometric ferrous oxide. *Metallurgical and Materials Transactions A*, 42(8):2259-2263. https://doi.org/10.1007/s11661-011-0652-9

Peng ZW, Hwang JY, Kim BG, et al., 2012. Microwave absorption capability of high volatile bituminous coal during pyrolysis. *Energy & Fuels*, 26(8):5146-5151. https://doi.org/10.1021/ef300914f

Rajendran S, Khan MM, Gracia F, et al., 2016. Ce^{3+}-ion-induced visible-light photocatalytic degradation and electrochemical activity of ZnO/CeO_2 nanocomposite. *Scientific Reports*, 6:31641. https://doi.org/10.1038/srep31641

Robati D, Mirza B, Rajabi M, et al., 2016. Removal of hazardous dyes-BR 12 and methyl orange using graphene oxide as an adsorbent from aqueous phase. *Chemical Engineering Journal*, 284:687-697.
https://doi.org/10.1016/j.cej.2015.08.131

Sadhukhan AK, Gupta P, Saha RK, 2011. Modeling and experimental investigations on the pyrolysis of large coal particles. *Energy & Fuels*, 25(12):5573-5583.
https://doi.org/10.1021/ef201162c

Saleh TA, Gupta VK, 2011. Functionalization of tungsten oxide into MWCNT and its application for sunlight-induced degradation of rhodamine B. *Journal of Colloid and Interface Science*, 362(2):337-344.
https://doi.org/10.1016/j.jcis.2011.06.081

Saleh TA, Gupta VK, 2012a. Photo-catalyzed degradation of hazardous dye methyl orange by use of a composite catalyst consisting of multi-walled carbon nanotubes and titanium dioxide. *Journal of Colloid and Interface Science*, 371(1):101-106.
https://doi.org/10.1016/j.jcis.2011.12.038

Saleh TA, Gupta VK, 2012b. Synthesis and characterization of alumina nano-particles polyamide membrane with enhanced flux rejection performance. *Separation and Purification Technology*, 89:245-251.
https://doi.org/10.1016/j.seppur.2012.01.039

Saleh TA, Gupta VK, 2014. Processing methods, characteristics and adsorption behavior of tire derived carbons: a review. *Advances in Colloid and Interface Science*, 211:93-101.
https://doi.org/10.1016/j.cis.2014.06.006

Saravanan R, Thirumal E, Gupta VK, et al., 2013a. The photocatalytic activity of ZnO prepared by simple thermal decomposition method at various temperatures. *Journal of Molecular Liquids*, 177:394-401.
https://doi.org/10.1016/j.molliq.2012.10.018

Saravanan R, Gupta VK, Prakash T, et al., 2013b. Synthesis, characterization and photocatalytic activity of novel Hg doped ZnO nanorods prepared by thermal decomposition method. *Journal of Molecular Liquids*, 178:88-93.
https://doi.org/10.1016/j.molliq.2012.11.012

Saravanan R, Karthikeyan N, Gupta VK, et al., 2013c. ZnO/Ag nanocomposite: an efficient catalyst for degradation studies of textile effluents under visible light. *Materials Science and Engineering: C*, 33(4):2235-2244.
https://doi.org/10.1016/j.msec.2013.01.046

Saravanan R, Joicy S, Gupta VK, et al., 2013d. Visible light induced degradation of methylene blue using CeO_2/V_2O_5 and CeO_2/CuO catalysts. *Materials Science and Engineering: C*, 33(8):4725-4731.
https://doi.org/10.1016/j.msec.2013.07.034

Saravanan R, Khan MM, Gupta VK, et al., 2015a. ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents. *Journal of Colloid and Interface Science*, 452:126-133.
https://doi.org/10.1016/j.jcis.2015.04.035

Saravanan R, Khan MM, Gupta VK, et al., 2015b. ZnO/Ag/Mn_2O_3 nanocomposite for visible light-induced industrial textile effluent degradation, uric acid and ascorbic acid sensing and antimicrobial activity. *RSC Advances*, 5(44):34645-34651.
https://doi.org/10.1039/C5RA02557E

Saravanan R, Sacari E, Gracia F, et al., 2016. Conducting PANI stimulated ZnO system for visible light photocatalytic degradation of coloured dyes. *Journal of Molecular Liquids*, 221:1029-1033.
https://doi.org/10.1016/j.molliq.2016.06.074

Shuang Y, Wu CN, Yan BH, et al., 2010. Heat transfer inside particles and devolatilization for coal pyrolysis to acetylene at ultrahigh temperatures. *Energy & Fuels*, 24(5):2991-2998.
https://doi.org/10.1021/ef9015813

Sun X, 2006. Treatment of Electric Arc Furnace Dust by Microwave Heating. PhD Thesis, Michigan Technological University, Michigan, USA.

Zeaiter J, Azizi F, Lameh M, et al., 2018. Waste tire pyrolysis using thermal solar energy: an integrated approach. *Renewable Energy*, 123:44-51.
https://doi.org/10.1016/j.renene.2018.02.030

Zhou J, Yang YR, Ren XH, et al., 2006. Investigation of reinforcement of the modified carbon black from wasted tires by nuclear magnetic resonance. *Journal of Zhejiang University SCIENCE A*, 7(8):1440-1446.
https://doi.org/10.1631/jzus.2006.A1440

Zhu WK, Song WL, Lin WG, 2008. Effect of the coal particle size on pyrolysis and char reactivity for two types of coal and demineralized coal. *Energy & Fuels*, 22(4):2482-2487.
https://doi.org/10.1021/ef800143h

中文概要

题　目：高效绿色的微波热解废旧轮胎方法

目　的：废旧轮胎正成为一个日益严峻的环境问题。本文旨在研究发掘一个高效绿色的处理废旧轮胎的方法。本文探讨微波热解废旧轮胎的可能性，同时研究不同环境温度、微波频率以及样本大小对微波热解废旧轮胎效率的影响。

方　法：1. 通过实验分析，验证影响微波热解废旧轮胎的关键因素，同时找出微波热解废旧轮胎的最佳条件。2. 理论设计多个与分解效率相关的变量，推导其计算公式，从而证明提高热解效率的关键因素。3. 分析热解后产物，证明该方法是高效绿色的。

结　论：1. 微波热解废旧轮胎的最佳条件是：轮胎样品厚度为 5 mm、微波频率为 915 MHz 以及环境温度为 592.1 °C。2. 分解产物中包含 35%的炭黑、40%的原油以及 25%的可燃性气体；这证明微波热解法是有效的。3. 所有产物皆可重复利用，证明该方法是高效绿色的。

关键词：循环系统；废旧轮胎；微波；热解；炭黑；油；天然气