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Characteristics of limonene formation during microwave pyrolysis of scrap tires and quantitative analysis

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ABSTRACT

Using the test system for the microwave pyrolysis of scrap tires, the effects of different factors on the production characteristics of limonene in oils were investigated. The results showed that the optimum processing parameters for the production of limonene were the specific microwave power of 15 W/g, the weight hourly space velocity of 3.75 h^{-1}, the tire particle size of 0.6 mm, and the absence of steel wires. The yield of limonene in the pyrolysis oil under this set of conditions was up to 23.4%. According to the pyrolysis process and the product composition, the mechanism of limonene production under microwave pyrolysis conditions was predicted. The content of limonene in the pyrolysis oil was quantitatively analyzed by an external standard method (ESM) and the peak area normalization method (PANM) separately. The numerical values of the test results obtained by multiplying PANM by the calibration factor of 1.5 equal the corresponding results obtained using the ESM method. Compared with conventional pyrolysis, the microwave pyrolysis of waste tires has a higher yield of limonene under optimized conditions. The results provide an important reference for the high-value utilization of waste tires and the utilization of resources, especially the subsequent production of limonene.

1. Introduction

Limonene is a kind of light yellow liquid with the pleasant aroma of orange peel. It can be widely used in chemicals, food, spices, and medicines. It can be used as an antioxidant, a preservative, and a perfume additive, and also for the synthesis of chemical fragrances such as carvone and menthol [1]. It has been widely used in medicine, and can effectively treat different types of cancer. In addition, limonene can also be used as non-water solvents, pesticides, etc. [2]. Depending on the purity level, the limonene market price is about 1500–2500 US dollars/ton. It can be seen that limonene has a wide range of applications and a high economic value.

Limonene is widely found in natural plant essential oils. Traditional limonene is extracted from citrus or orange peel by using a solvent, steam distillation, supercritical extraction, and microwave extraction [3]. In steam distillation, due to the high temperature boiling for long time, the fragrance component can easily be oxidized or hydrolyzed, and the extraction rate is low. The solvent method and other extraction methods cannot be performed without an organic solvent. The organic solvents residue in the product can affect product quality. Also, the recycling of waste organic solvents requires good technology and high costs, and the discharged extract can also cause environmental pollution. Therefore, the traditional methods of production of limonene have some drawbacks, and the options for the source of raw materials are relatively narrow.

In recent years, the study of pyrolysis of waste tires show that the content of limonene in the pyrolysis oil of tires is very impressive [4–9], and some even reach up to 20%, which could be a new way to produce limonene efficiently. The yield of limonene is significantly affected by the pyrolysis temperature. The temperature range suitable for the pyrolysis is about 400–500 °C [4–8]. Roy et al. obtained limonene yields of up to 5.0 wt% in the pyrolysis oil by using a fixed bed reactor at a pyrolysis temperature of 500 °C [10]. Zhang and others also obtained a similar limonene yield using

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vacuum pyrolysis. The limonene yield in the pyrolysis oil was 4.9 wt% at 500 °C [11]. A further increase in the temperature leads to a decrease in the yield of limonene because the chemical properties of limonene are unstable, and it easily decomposes into trimethylbenzene, cymene, and indene at higher temperatures [12]. In addition, the tire type, reactor pressure, catalyst, and other factors also have a certain impact on the limonene yield [8,9,13].

Unlike in the traditional heating methods, microwaves can pass through the feedstock and cause evenly volumetric temperature change by inducing dipole rotation of molecules; as a result, the temperature gradient is reduced inside the samples. Because rubber is a bad conductor of heat, the traditional heating methods have low heat conduction efficiency, and can easily produce a large temperature gradient and local high temperature, which can induce material coking. These issues become the main obstacle to the continuous operation of pyrolysis [14]. In contrast, for the microwave heating technology, the internal temperature field of the material is relatively uniform and the temperature gradient is small during the pyrolysis process. The primary product avoids the high temperature region during the migration process, which reduces the occurrence of secondary reaction, thus reducing the decomposition of limonene. Also, because the temperature is more uniform, the coking problem during traditional pyrolysis process, which limits the continuous operation of pyrolysis, can potentially be mitigated. It is noteworthy that carbon black (25%–35% of tire) is also an important component of tires. During microwave treatment, carbon black can be regarded as the “internal heat source” due to its splendid absorbance of microwaves, which can accelerate the pyrolysis reaction of tires [15,16]. In addition, the steel wire in the tire is subject to discharge in the microwave field, and the resulting high temperature and plasma atmosphere greatly promote the degradation of materials [17]. The study also found that microwave pyrolysis (MP) significantly reduced the activation energy of the pyrolysis reaction compared with conventional pyrolysis (CP) [18], which is expected to reduce the overall pyrolysis temperature of feedstocks and is more favorable for the production of limonene.

At present, the research on limonene in pyrolysis oil of waste tires is mainly focused on the influence of a single factor, and the optimal reaction conditions for maximizing limonene yield are not studied systematically. Most of the studies are performed under normal heating conditions, and the precipitation characteristics of limonene under microwave pyrolysis conditions have not yet been systematically explored. In addition, for the quantitative analysis of the components of pyrolysis oil, the quantitative methods used are usually the peak area normalization method (PANM), internal standard method, external standard method (ESM), and standard addition method [19]. The external standard method can be used for quantitative analysis of the unknown sample under exactly the same conditions based on the working curve of the standard samples. The result is accurate and targeted [19], which can be used as the benchmark of other methods. In the literature, the peak area normalization method is mostly used when calculating the percentage of limonene in the pyrolysis oil. This method is relatively simple. However, since the response factor (the amount of sample represented by the peak unit area) of different compounds under the same conditions and on the same detector are usually different, this method is only used when the samples are in a homologous series or only for approximate quantitative analysis.

Therefore, the purpose of this study is to investigate the effects of different factors (microwave power *P*, weight hourly space velocity *WHSV*, tire particle size *d*, presence of steel wires) on the yield of limonene via the process of microwave pyrolysis of waste tires, and to explore the production and enrichment of limonene. Considering the microwave parameter only applicable to the facility employed in most research work, instead, we use the power per 1 g sample as a new criterion, i.e., the specific microwave power (*SMP*). According to the test and product analysis results, the production of limonene and the corresponding reaction mechanism were determined. In addition, the absolute concentration and content of limonene in the pyrolysis oil were quantitatively determined by the external standard method. The peak area normalization method was also used for comparative analysis to evaluate the reliability of the existing quantitative analysis method. This study proposes a new method for the efficient extraction of limonene from waste tires, and provides a reference for the industrial application of this technology, which has important research significance and potential application value.

2. Test systems and methods

2.1. Test raw materials

The sample used in this experiment was acquired from Youhao environment company at Zouping County, China. There are two kinds of raw materials: One is in powder form obtained by crushing the tires and removing the steel wires, and the average particle size is $d = 0.6$ mm. The other is in the form of tire blocks obtained by removing the steel wires and cutting evenly into 10 mm × 10 mm × 10 mm and 30 mm × 30 mm × 30 mm blocks. The powder sample was obtained from the whole rubber tire and the block was obtained from the side of the rubber tire. Table 1 shows the results of the proximate and ultimate analyses of samples. It can be found that the difference in composition and content between these two kinds of samples is very small, so the influence of the composition on the pyrolysis process and the products is negligible and can be ignored.

M, A, V and FC refer to the moisture, ash, volatile and fixed carbon content on an air dried basis, respectively; C, H, N and S refer to the carbon, hydrogen, nitrogen, and sulfur content on an air dried basis, respectively; LHV means the lower heating value.

2.2. Test systems and methods

A schematic diagram of the microwave pyrolysis system is presented in Fig. 1. It mainly consists of a microwave oven, a quartz reactor (60 mm outer diameter and 130 mm length) and a products collection unit, as our previous studies showed [21,22]. The microwave oven (Media M3-L233C) with the maximum output power of 900 W, can be operated in a continuous manner without the usual intermittent heating. This ensures that the media is being heated continuously and the internal temperature distribution

Table 1
Results of proximate and ultimate analyses of feedstocks.

Raw material	Proximate analysis ω/%				Ultimate analysis ω/%				LHV/(kJ·kg^{-1})
	M	A	V	FC	C	H	N	S	
Tire powder	0.58	7.83	61.29	30.30	80.91	7.22	0.45	1.53	39815
Tire block	0.67	7.39	62.03	29.91	80.11	7.45	0.41	1.22	38297