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Overview of High-Value Reuse and Grinding at Sub-Zero Temperature of Scrap Rubber Tires

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Overview of High-Value Reuse and Grinding at Sub-Zero Temperature of Scrap Rubber Tires

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Abstract. It is of good application prospects for the low carbon remanufacturing process to product fine reclaimed rubber powder by grinding scrap rubber tire at low temperature. Through review of the recycling technology of scrap tire at low temperature and the high-value reuse of the regenerated rubber powder of domestic and abroad, the advantages and disadvantages of several grinding processes at low temperature are compared, the main existing problems of the cryogenic grinding technology are put forward. In addition, the development trend of the cryogenic grinding technology of waste tire and the high-value reuse of the regenerated rubber powder is prospected. The key point to solve the problem of high-value reuse is to improve the manufacturing process of fine reclaimed rubber powder and the development of equipment.

1. Introduction

The number of vehicles in China reached 310 million in 2017. Among them, there are 217 million cars. It is estimated that the number of scrap tires would be 379.8 million in 2018, and the weight would be 14.59 million tons. And it will grow about 5%-6% annually. It has attracted more and more attentions that how to recycle waste tires [1].

There are several ways to recycle waste tires [2], the most valuable way is to crush them into rubber powder and to recycle them in order to become new value product. Among the ways to crush waste tires, they are divided into grinding at room temperature and grinding at cryogenic temperature.

At room temperature, it is not easy to crush the elastomeric rubber tires which is easily deformed by heating and the material whose viscoelastic behavior will lead to plastic deformation in the process of mechanical force. At low temperatures brittle fracture can occur easily (as brittle as glass) if the material is subjected to and then crushed. In order to produce high value fine rubber powder, the cryogenic grinding technology will lead to the recycling process of scrap tires in the future.

2. Cryogenic Grinding Technology of Waste Tire

Cryogenic grinding is a process to comminute brittle materials (tires, rubber and other elastic materials) by use of the characteristics of brittleness of materials at low temperatures (such as tires in 193K become very brittle and easy to comminute or separate) [3]. Cryogenic grinding can produce more finely crumb powder than normal grinding, and fine rubber powder is of high value-added [4]. At present, the cryogenic grinding methods of scrap tires (according to the different cold sources) mainly divided into the cryogenic grinding technology with liquid nitrogen, with air expansion refrigeration, with LNG (liquefied natural gas) cold energy refrigeration and so on. The scrap rubber tire blocks are crushed in cold brittleness condition, after they are cooled in refrigeration equipment [5].



2.1. Cryogenic Grinding Technology with Liquid Nitrogen

Cryogenic grinding technology with liquid nitrogen is a kind of technology which uses liquid nitrogen as cooling medium to lower scrap tire below the critical glass state temperature for comminution. As the boiling point of liquid nitrogen is 77K, it is easy to cool down the material below the glass state temperature [6]. In addition, as an inert substance, liquid nitrogen can prevent the material from being oxidized in severe comminution processes.

At present, cryogenic grinding processes with liquid nitrogen for scrap tires are mainly divided into two types: One is to freeze the tire directly to the glass state temperature with liquid nitrogen. Another is to crush the tire into a certain size of rubber block at room temperature and then freeze it with liquid nitrogen below the glass state temperature before grinding. Compared the two processes, the second one is more economical and energy-saving.

2.2. Sub-Zero Grinding Technology with Air Expansion Refrigeration

It is proved that the friction heat generated from the grinding can be counteracted when the temperature of the rubber is about 193K [7]. Based on this point of view, in order to improve the economic feasibility of sub-zero grinding of waste tires and reduce the grinding cost, the sub-zero grinding technology using air expansion refrigeration has been developed. The main raw material comes from air which is abundant resources, non-polluted. Besides it is of effective refrigeration at low cost. The basic principle of the sub-zero grinding technology is to compress the air to a certain pressure and produce low temperature air below 153K by gasification and expansion of turbine, and then this low temperature air is used as a refrigerant. The sub-zero grinding process of air expansion refrigeration mainly operate sequentially at environment temperature and at sub-zero temperature.

2.3. Cryogenic Grinding Technology with LNG (liquefied Natural Gas) Cold Energy Refrigeration

With the development with LNG industry, the utilization of LNG cold energy has attracted people's attention. Compared with the traditional cryogenic grinding technology, the cryogenic grinding technology with LNG cold energy refrigeration is of lower cost [8]. LNG is a liquid gas at 111K cryogenic temperature under atmospheric pressure, which will release a large amount of cold energy when it gasifies. The released cold energy can be used as a refrigerant when the scrap tires are comminuted at low temperature, so as to prevent the waste of cold energy.

There are two kinds of cryogenic grinding processes using LNG cold energy as refrigerant: one is to produce liquid nitrogen as refrigerant; the other is to directly recover the cold energy of LNG by using nitrogen as refrigerant.

The advantages and disadvantages of the above cryogenic grinding technology are compared in Table 1.

Table 1. Comparison of several low temperature grinding methods (Different cold source).

Methods	Advantages	Disadvantages
Liquid nitrogen refrigeration	<i>The boiling point is 77K, the refrigeration effect is good, and the precooling time is short., and liquid nitrogen can prevent oxidation as an inert material.</i>	<i>The refrigerant consumption is much large and the cost is high.</i>
Air expansion refrigeration	<i>Making full use of cooling capacity and dry air, rubber does not need to freeze to about 168K of embrittlement temperature and low power consumption.</i>	<i>A large amount of refrigeration equipment is needed</i>
LNG cold energy refrigeration	<i>Cold energy released directly by LNG during gasification reheat process, Less waste caused by cold energy emissions.</i>	<i>Large investment and low energy consumption</i>

3. Current R&D and Future Development Trend

The industrialization of cryogenic grinding technology first came true in 1948, the first company that achieved and utilized liquid nitrogen cryogenic commercial grinding is LNP in America [9].

3.1. R&D Status Abroad

Liquid nitrogen cryogenic grinding has the benefits of having short pre-cooling time, ample material of cold source and so on, which is the prime way to comminute junk tires in developed countries. The American invented this method in advance, which came up with a device that is able to smash plastic and rubber by means of cryogenic grinding with liquid nitrogen in 1960: it pre-cool plastic or rubber with liquid nitrogen at first, and then transport them to grinder by spiral conveyor [10].

According to the patent [11], they put rubber into a grinding equipment below the glass state temperature, and simultaneously add cryogen (such as liquid nitrogen) for cryogenic grinding.

UCC is one of the earliest companies to utilize the technology of cryogenic grinding in the world, whose product line of fine rubber powder has developed from the first generation to the fifth at present [12]. The whole process is sound environmentally. The 5th generation product line adopts the technology of 77k sub-zero treatment. The processes of grinding of junk tires consist of input, crushing, cooling grinding of the whole tire and separating steel wires and fiber from rubber tires, through which the degree of purity of rubber powder can reach up to 99.99%.

It was exploited by Institute of cryogenic physical engineering of the National Academy of Sciences of Ukraine that preparation technology of rubber powder by cryogenic grinding waste tires with liquid nitrogen [13]. The main processes of crushing and grinding are performed at cryogenic temperature, which can manufacture rubber powder with particle size of 0.05-1.25mm according to the needs of the market.

3.2. Domestic R&D Status

The production of waste rubber powder in China started commercial production and application in 1980s. In the early 1990s, it came to an active period. After several decades of development, it has been equipped with certain capacity to manufacture rubber powder.

But the technology of cryogenic grinding in China started relatively late. Due to the high cost, it has not been industrialized in the development. In the 1990s, the first cryogenic grinding with air expansion refrigeration was developed independently in China, which is of the merits of abundant cold source and non-polluted, compared with other cryogenic grinding methods.

China has made a series of improvement as following on the base of cryogenic grinding technology: the cryogenic grinding method with electric pulse was researched by W Wu etc. [14], which makes high voltage electric current pulse in liquid nitrogen for discharging, thus trigger liquid-electric effect to crush waste rubber. Meanwhile, Qingdao green leaf Rubber Co. Ltd and Shenzhen Institute of mechanical and electrical technology jointly exploited LY cryogenic method with liquid nitrogen [13]. The rubber powder with particle size of 75-180 μ m could be obtained by this method. Zhao B invented a kind of waste tire cryogenic product line. The size of the rubber powder produced under the product line is below 120 mesh, and the purity can reach more than 99.7%[15].The related cryogenic grinding processes also be investigated by the 609th Research Institute of Chinese Aviation Industry [16] [17], Cryogenic Technology Experimental Centre of Chinese Academy of Sciences [18], and Dalian University of Technology.

3.3. Prospect of Development Trend

Compared with developed countries such as Europe and the United States, the normal grinding technology of rubber powder still occupies a dominant position in the domestic production process. However, the proportion of the rubber powder with high added value is still not high. For the sake of efficiently recycling of waste tire, it is preferable to make fine rubber powder by grinding at low temperature currently.

Compared with grinding rubber powder at normal temperature, cryogenic grinding method requires more investment and energy consumption. However, the cryogenic grinding technology with the air expansion refrigeration and LNG cold energy described above has provided a new way to prepare fine rubber powder at low temperature and low cost. At the same time, liquid nitrogen refrigeration has obvious advantages such as good refrigeration effect, preventing rubber oxidation and low power required for grinding. However, the consumption of liquid nitrogen in grinding waste tires with liquid nitrogen refrigeration is still much large. One of the key factors to be solved is how to reduce the consumption of liquid nitrogen or its production cost.

Because of the advantages of fine rubber powder prepared from waste rubber at cryogenic temperature, it is of great significance to the high value application of waste tires. It is an economical and efficient method to produce fine rubber powder combined at room temperature and at cryogenic temperature. Nowadays, environmental protection is paid to more and more attention, the cryogenic grinding method, as a clean and pollution-free process, will deserves to be favored by people.

4. High Added-Value Reuse of Fine Reclaimed Rubber Powder

For the high-value reuse of fine recycled rubber powder, one way is used in the production of new tires, in which part of the recycled rubber powder instead of the original rubber powder. Due to the high purity, small particle size and non-pollute of the rubber powder produced by cryogenic grinding, it can be used in some important products to achieve high-value return. For example, it will greatly improve the performance of automobile tires and reduce the production cost if the raw rubber powder is instead of about 20% fine recycled rubber powder obtained by cryogenic grinding [19].

In the 172nd meeting of the rubber society of the American Chemical Society, the latest study released that [20]: the smaller the size of rubber particles, the better the positive effect on physical properties. the rubber powders can be used to manufacture new thermosetting rubber complexes. The application of rubber powder with different numbers to different occasions is shown in Table 2 below:

Table 2. Application of different mesh rubber powder

Methods	Particle size of rubber powder	Application
Cryogenic grinding	40~60 mesh (fine rubber powder)	Rubber filled products, rubber modified products.
	60~80 mesh (fine rubber powder)	Automobile tires, rubber products, building materials
	80~200 mesh (micro powder)	Rubber products, military products

Another high-value reuse for the new energy automotive industry is to explore further extraction of carbon black materials from recycled rubber powder for lithium battery capacitors. A low temperature pyrolysis process made of recycled rubber powder was developed by Delta Energy Company in the United States, which can recover carbon black-based solids from used tires rubber and reduce the production amount of harmful polycyclic aromatic hydrocarbons. Its quality is equivalent to that of carbon black directly produced. The calculation shows that the net energy recovery value of the process is higher than that of the traditional process.

In addition, a new system producing electricity was developed by Israel from used tires, which sells electricity generated by combustion to the State Grid. At the same time the by-products such as steel and sulphur are also obtained. The whole process is safe, clean and pollution-free.

It is put forward to by Z Li of Qingdao University of Science and Technology that the idea of used rubbers can be cracked and high-value reuse of its pyrolysis products can be utilized [21]. It is believed that the microwave pyrolysis technology of used rubber has the advantages of fast cracking speed, high product quality, low energy consumption and no pollution., It can realize automation and mass production.

Chinese government is stepping up to support the new products that are environmental, efficient and energy-saving. The fine rubber powder of high value-added will be the main way of recycling used tires. It will become the development goal of used tire recycling industry that utilizes high quality recycled rubber powder to promote the replacement of synthetic rubber and natural rubber to achieve the goal of saving resources.

5. Summary and Prospect

The recycling of scrap tires is of great value. It not only protects the environment, but also makes reasonable use of waste materials. There is higher utilization value for the fine recycled rubber powder produced by cryogenic grinding than coarse powder produced at room temperature. The technology of sub-zero grinding has been studied deeply at home and abroad, however, it has not been industrialized promotion in China.

Although the rubber powder produced by cryogenic grinding of waste tires has the characteristics of fine particle size and low oxidation degree, the cold source is an obstacle to realize freezing scrap tires grinding. Because cold source is directly related to the cost whether it is worthy of cryogenic grinding. Therefore, the efficient refrigeration technology, development of cryogenic grinding equipment and optimization of cryogenic grinding process are the keys of future research in order to improve the economic feasibility of cryogenic grinding, which is also an important prerequisite for promoting cryogenic grinding technology.

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