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Experimental study on utilization of waste heat cracking rubber powder from blast furnace slag in fluidized bed equipment

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Abstract

After the high temperature slag particles made by dry granulation are used as heat in order to deal with the problems of insufficient utilization of waste heat and large volume of waste tires. A new idea of producing cracking oil, gas and carbon black by cracking rubber powder based on fluidized bed equipment was put forward to realize waste utilization, energy saving and environmental protection. The waste heat when the liquid blast furnace slag is granulated into high temperature particles is used as free heat source, and the cracking gas is used as heat carrier to transfer heat into the fluidized bed to realize the joint production of oil and gas. The process flow was designed and the influencing factors in the fluidized cracking process of rubber powder were analyzed, including cracking temperature, particle size of rubber powder, residence time and catalyst. It was found that when the cracking temperature was 550 degrees, 35% NaOH was used as catalyst and the residence time was 2 seconds, the highest oil yield was 51%. The smaller the particle size of rubber powder, the larger the ratio of cracking gas in the product. The yield of cracking gas can be improved when the blast furnace slag is used as catalyst, while the use of Fe powder and CaO catalyst can increase the ratio of carbon black in the product.

Keywords

Used tires; waste heat recovery; the catalyst; fluidized bed; blast furnace slag.

As the "black pollution" in today's society, waste tires have brought huge disasters to the entire society. The number of them is increasing every year, and it is difficult to be degraded by nature normally, which brings tremendous pressure to the natural environment and even the survival of human beings. Used tires are a kind of solid waste with huge potential, which is called "potential oil field" and "urban minerals", [1]. Therefore, the use of high-efficiency and energy-saving methods to turn waste tires into valuables and realize the efficient use of waste tires can not only greatly reduce environmental pollution, but also have important significance for the realization of green economy and sustainable development.

The blast furnace is the main by-product in the iron and steel production process, and its production process contains a large amount of surplus resources. The consciousness of every ton of pig iron slag will be accompanied by 0.3t-0.6t slag by-products, that is, about 15kg-18kg [2-3]. The treatment of today's high-temperature slag mostly adopts the method of flushing slag with water, which requires a lot of water resources and wastes a lot of resources. The energy center of the State Key Laboratory of Qingdao Technological University has done a lot of research on how to use the slag heat of high-temperature waste heat. The centrifugal granulation device developed by it can prepare high-

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temperature furnace slag particles into high-temperature slag particles. Its diameter is within 10mm, and the temperature is 800 to 1,000°C [4].

In this paper, the waste heat of slag particles is used as a free source to fluidize waste particles. The powder gas is used as a heat carrier to pass into the fluidized bed to fluidize the glue and produce growth oil, gasoline gas, carbon black and other products. resistance.

1. Experimental materials and methods

1.1 Experimental materials

Dawang Group provided the rubber powder raw materials needed in the experiment, and the physicochemical properties and properties are shown in Table 1. It is contacted by a galactagogue through a multi-magnetic level. During the rupture process, lead and other substances are removed through mineral processing. The particle size of the granular rubber powder after rupture can be controlled between 40 and 120 meshes. Figure 2 is 40 mesh and 60 mesh. , 80 mesh, 100 mesh and 120 mesh granular rubber powder particles macro photos.

Fig 1. Used tire crusher

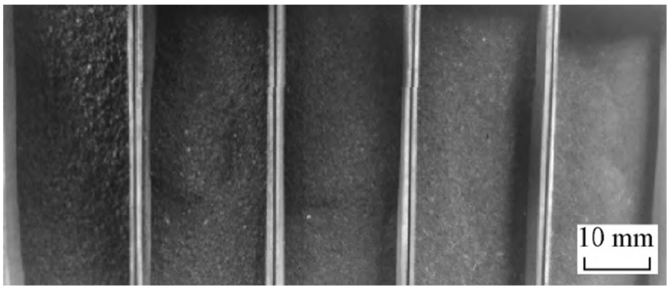

Fig 2. Powder particles

Table 1. Physical and chemical properties of wheel rubber powder

Performance item	Rubber powder model/mesh						
	200	160	120	100	80	60	40
The average particle size /um	74	96	119	140	173	221	381
Screen specifications / (mesh /in)	200	160	120	100	80	60	40
Screening rate /% ≥	95	95	95	95	95	95	95
Moisture /% ≤	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ash /% ≤	10	10	10	10	10	10	10
Acetone extract /% ≤	15	15	15	15	15	15	15
Metal content /%	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Rakushin strength /MPa ≥	--	--	--	--	16	13	8
Fracture elongation rate /%	--	--	--	--	500	500	450
density /(g/cm3)	All are black homogeneous powder, all between 1.10-1.13						

Note: lin= 2.54cm

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The blast furnace slag comes from the fourth blast furnace of Qinggang Group. The high-temperature blast furnace slag particles are prepared by the laboratory's self-made dry centrifugal granulation device (Figure 3). The particle size distribution is shown in Table 2:

Table 2. Distribution of blast furnace slag particle size %

Blast furnace slag particles	<2mm	2mm-4mm	4mm-6mm	6mm-8mm	8mm-10mm
Percentage	54. 21%	21. 03%	18. 36%	2. 13%	4. 36%

Fig 3. BF slag

1.2 Experimental technology, invention devices and products

1.2.1 Pyrolysis process

Figure 4 is a process flow diagram of using blast furnace slag waste heat to fluidize tire rubber powder. The liquid blast furnace slag is granulated by the centrifugal granulation device and then enters the heat exchange device to replace the heat with the cracked gas. After the heat exchange, the temperature of the cracked gas is 450-800 degrees, and can be controlled within the temperature range of 450-800 degrees through the control system Regulation. As the heat carrier, the pyrolysis gas is pressurized by a high-temperature pressurized fan and then passed into the fluidized bed reactor; the tire rubber powder enters the fluidized bed reactor from the screw feeder; the gas product enters the cyclone separator, and the cyclone separator removes the carbon The black and unremoved impurities are separated. Part of the separated gas product is controlled by the split control valve to enter the condenser, and the other part enters the heat exchange device as fluidized gas; the gas entering the condensing device is condensed to produce pyrolysis oil and stored in the pyrolysis tank , The non-condensable pyrolysis gas is stored in the gas storage tank. During the experiment, 30g rubber powder enters the fluidized reaction zone slowly from the screw feeder within 1 minute, and the fluidization wind speed is 1.79m/s to ensure that the rubber powder is in a suspended fluidized state. At this time, the fluidization effect is the best and the heat exchange efficiency is the highest. , After the reaction, measure the content of each component in the oil storage tank, gas storage tank, and slag storage tank to analyze the composition of each part.

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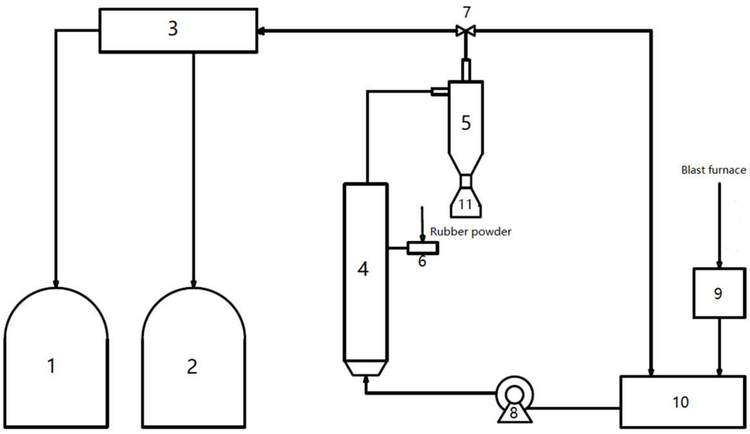

1—gas storage tank; 2—oil storage tank; 3—cooler; 4—fluidized bed reactor; 5—cyclone separator; 6—rubber powder screw feeder; 7—diversion control valve; 8—circulation fan 9—Blast furnace slag granulation device; 10—Blast furnace slag heat exchange device; 11—Slag storage tank

Fig 4. Process flow chart of waste tire pellet cracking by waste heat from blast furnace slag

1.2.2 Cracking device

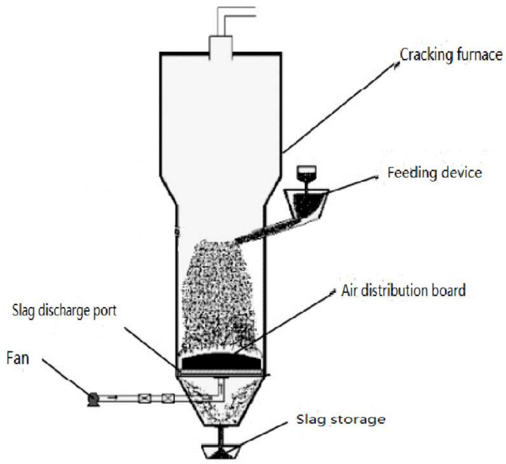

Fig 5. Overall structure diagram of fluidized bed for cracking tire particles with blast furnace slag waste heat

Figure 5 shows the specific structure of the fluidized bed reactor. The upper end is equipped with a rubber powder screw feeding device, and the bottom is a slag storage for collecting carbon black and other impurities. The cracked gas is sent by a fan to blow up the rubber powder and make it suspended In a fluidized state, the entire device is sealed, and the pyrolysis oil and pyrolysis gas produced by the cracking are discharged from the upper end into the cyclone separator behind.

1.2.3 Cracked product

(1) Pyrolysis gas

The pyrolysis gas produced in the cracking process has a calorific value of 46.2 MJ/kg, which is non-condensable dry gas, mainly composed of hydrocarbon gas, butadiene, CO2, H2 and other gases with high calorific value, and can be used for gas-fired power generation.

(2) Pyrolysis oil

After tire cracking, the calorific value can be as high as 40MJ/kg, and it contains a lot of sulfur, nitrogen, and polyaromatic hydrocarbon compounds. It has high economic value and has a certain corrosive effect. The cracked oil undergoes subsequent hydrorefining After adjustment, it can reach the standard of automotive diesel.

(3) Carbon black

Carbon black accounts for 35% of tire pyrolysis, its calorific value is 30MJ/kg, and its carbon content is 80%. It has a wide range of uses and has high economic value. For example, it can be used as a filler in rubber products in the rubber industry; Used as color masterbatch for part of pigment carbon black, and can be used as pigment offset printing ink in the offset printing ink industry.

2. Results and discussion

2.1 The influence of temperature on the distribution of rubber powder pyrolysis products

During the cracking process of waste tire rubber powder, various factors such as the reaction temperature, the size of the rubber powder particle size, the residence time, the catalyst, and the rapid heating up have a great influence on it [5]. Is the reaction temperature. After thermogravimetric analysis of the rubber powder particles [6], the pyrolysis reaction no longer proceeded when the reaction temperature was >460°C. Most studies have shown that when the reaction temperature is between 500°C and 700°C, the increase in temperature has almost no effect on the pyrolysis behavior of waste tires. Therefore, this experiment stipulates that the feed amount must be 30g, and the changes in the fluidized pyrolysis products of rubber powder under different temperatures (450°C, 500°C, 550°C, 600°C, and 650°C) were studied. The results are shown in Table 3. Shown.

Table 3. The influence of temperature on the distribution of rubber powder pyrolysis products %

	450℃	500℃	550℃	600℃	650℃
Pyrolysis oil	36.3	45.5	46.4	45.8	45.1
Pyrolysis gas	9.4	9.8	10.7	13.8	15.2
Carbon black	54.3	44.7	42.9	40.4	39.7

It can be seen from Table 3 that the output of pyrolysis oil first increases with the increase of temperature, then decreases with the increase of temperature, and reaches the maximum value of 46.4% at 550℃, while the content of pyrolysis gas increases with the increase of temperature. Increased, from 9.4% to 15.2%, while the output of carbon black decreased with the increase in temperature, from 54.3% to 39.7%.

The endothermic reaction is the main form of the rubber powder cracking process. Driven by an external heating source, the C—H bond in the tire rubber powder is more likely to break quickly. As the temperature rises, the energy provided by pyrolysis gradually increases. The pyrolysis reaction of rubber powder is also easier to proceed [10]. The cracking reaction progresses more and more thoroughly with the increase of temperature. The higher the temperature under the premise that other conditions remain unchanged, the more intense the secondary reaction such as dehydrogenation and decarboxylation. This reaction mainly generates low molecular non-condensable gas, so cracked gas The yield of pyrolysis oil increases with the increase of temperature; for pyrolysis oil, when the temperature rises, the secondary reaction intensifies, which will cause polymerization reaction between the olefin compounds in the cracked product and the low-carbon olefin compounds in the cracked gas. Increase the yield of pyrolysis oil [11], so the proportion of pyrolysis oil products in the range of 450℃-550℃ increases with the increase of temperature. When the temperature increases again (>550℃), the secondary reaction becomes more intense, the effect of the polymerization reaction is weakened, and the yield of pyrolysis oil decreases [12], so when the temperature is greater than 550℃, the proportion of pyrolysis oil products increases as the temperature rises. Shows a downward trend.

2.2 The influence of rubber powder particle size on the distribution of pyrolysis products

The rubber powders of different particle sizes provided by Dawang Group were selected, namely 40 mesh, 60 mesh, 80 mesh, 100 mesh, 120 mesh, the reaction temperature was controlled at 550 degrees,

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the feed rate was 30 g/min, and the wind speed was 2 m/s. Under this experimental state, explore the proportion of each experimental product in the total.

The smaller the rubber powder particles, the larger the specific surface area, the higher the heat and mass transfer rate during the pyrolysis process, and the better the fluidization effect. From Table 4, it can be seen that different purpose rubber powder particles can greatly affect the yield of pyrolysis products. . As the rubber powder particle size becomes smaller, the yield of pyrolysis oil and carbon black becomes lower, and the yield of pyrolysis gas becomes larger. When using 120 mesh rubber powder, the maximum yield of pyrolysis gas is 15.7%, at this time the yield of pyrolysis oil is 42.8%, and the yield of carbon black is 41.5%.

Table 4. The influence of rubber powder particle size on the distribution of pyrolysis products %

	40 mesh	60 mesh	80 mesh	100 mesh	120 mesh
Pyrolysis oil	49.2	48.3	46.4	44.2	42.8
Pyrolysis gas	6.4	8.2	10.7	13.1	15.7
Carbon black	44.4	43.5	42.9	42.7	41.5

The above situation occurs mainly because the influence of temperature on the rubber powder is from the outside to the inside. The larger the particle size, the later the internal heating time of the rubber powder, and the lower the heat transfer efficiency. This leads to the internal thermal cracking of the rubber powder particles At low temperature, the time of low-temperature pyrolysis will be longer, which will lead to the increase of incomplete pyrolysis solid products. Therefore, the larger the particle size of the rubber powder, the greater the proportion of carbon black products. When the rubber powder particle size is small, the internal and external temperature difference is small, the heat transfer rate is high, the temperature rises faster, and the cracking is complete. The generated cracking gas is easy to take away the small molecular organic matter that has not yet undergone the second cracking reaction, so the cracked oil The yield has decreased [13].

2.3 Effect of catalyst on the distribution of cracked products

Choose 40 mesh rubber powder, control the reaction temperature at about 550°C, and add 35% Fe2O3, NaOH, carbon powder, calcium oxide, iron powder, and blast furnace slag to the rubber powder particles. After the reaction, the proportion of products added with various catalysts was analyzed.

Table 5 shows the mass distribution of cracked oil, cracked gas and carbon black produced by the cracking of rubber powder after each catalyst is added. Blast furnace slag has high catalytic activity, mainly because the blast furnace slag particles contain substances such as iron trioxide, calcium oxide, and magnesium oxide.

Metal oxides can very well catalyze the cracking of gasification tar to enhance the conversion of low-molecular hydrocarbons in fuel gas. From Table 5, it can be seen that the use of blast furnace slag has a certain increase in the output of cracked oil and the cracking when calcium oxide is used as a catalyst. The oil production is not much different, but there is a big gap compared to the cracked oil yield obtained when NaOH is used as a catalyst. The highest yield of cracked oil is 53.5% when NaOH is used as the catalyst. The highest gas product obtained from C powder blending cracking is 17.6%.

Table 5. The influence of catalyst on the distribution of pyrolysis products %

	NaOH	CaO	Fe	Fe2O3	C	Blast furnace slag
Pyrolysis oil	53.5	49.2	36.2	32.2	40.1	46.5
Pyrolysis gas	15.2	13.0	14.3	17.4	17.6	17.2
Carbon black	31.3	37.8	49.5	50.4	42.3	36.3

2.4 The effect of residence time on the distribution of pyrolysis products

Because the fluidizing wind speed is constant, in order to adjust the residence time of the secondary reaction, increase the height of the fluidized bed reactor to increase the residence time. 40 mesh rubber powder is selected and 35% NaOH is added as a catalyst. The reaction temperature is controlled at about 550°C. Product distribution. The residence time increases according to the height of the

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fluidized bed reactor, increasing by 2 seconds, 4 seconds, 6 seconds, 8 seconds, 10 seconds, and 12 seconds respectively. The experimental results are shown in Table 6.

Table 6. The influence of residence time on the distribution of pyrolysis products%

	2s	4s	6s	8s	10s	12s
Pyrolysis oil	53.5	53.2	53.0	52.8	52.9	52.9
Pyrolysis gas	15.2	15.6	15.7	15.9	15.9	15.9
Carbon black	31.3	31.2	31.3	31.3	31.2	31.2

It can be seen that when the temperature is about 550℃, the increase of the residence time does not change the proportion of the product to a large extent. When the residence time increases by 2 seconds, the proportion of the cracked product does not change. With the increase of the residence time, the cracked oil The yield of pyrolysis gas decreased slightly, and the yield of cracked gas increased slightly, but when the residence time exceeded 8 seconds, the increase in the residence time did not change the proportion of products. In the whole process, the residence time has almost no effect on the proportion of carbon black. This is because at a temperature of 550°C, increasing the residence time of 2 seconds will not cause secondary reactions of volatiles. As the residence time increases, the secondary reaction of volatiles will increase, and the yield of pyrolysis oil will decrease and it will be converted into pyrolysis gas. The yield of carbon black is almost unaffected [15]; the effects of temperature and residence time on the secondary reaction of the pyrolysis volatiles of rubber powder are related to each other. Due to the limitation of temperature, the proportion of the product after the residence time exceeds 8 seconds There is no change.

3. Conclusion

(1) The yield of pyrolysis oil increases with the increase of temperature, reaching a maximum of 46.4% at 550 ℃, and then the yield of pyrolysis oil decreases with the increase of temperature; the smaller the rubber powder particles, the better the fluidization effect. The better the heat transfer effect between particles, the smaller the particle size of the rubber powder, the higher the gas yield in the pyrolysis product, but the lower the yield of pyrolysis oil and carbon black.

(2) Through the comparison of various catalysts, it is found that when NaOH is used as the catalyst, the yield of cracked oil is the highest at 53.5%; while when blast furnace slag is used as the catalyst, the yield of cracked oil decreases and the yield of cracked gas increases; calcium oxide, Iron powder improves the yield of solid carbon black.

(3) The residence time has a certain effect on the fluidized cracking of rubber powder. When the temperature is 550℃ and the residence time is within two seconds, since the volatile matter does not undergo a second gas phase reaction, the proportion of cracked products does not change significantly. With the increase of temperature and longer residence time, the secondary reaction intensifies, the yield of pyrolysis gas increases, and the yield of pyrolysis oil decreases. This test proved that: 550 ℃, rubber powder particles of 40 mesh, 35% NaOH as a catalyst, the highest yield of pyrolysis oil obtained within 2 seconds of residence time is 53.5%.

(4) Based on the principle of fluidized bed, it is conducive to the efficient recycling and pollution-free treatment of waste tires based on the waste heat of blast furnace slag.

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