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Research article

Xylene activation of coal tar pitch binding characteristics for production of metallurgical quality briquettes from coke breeze

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ABSTRACT

Coal tar pitch with xylene as activator was utilized to bind coke breeze to form a firm briquette at room temperature and xylene activation on binding behavior of the pitch was investigated. Furthermore, thermal behavior of the pitch and briquettes was studied to facilitate low temperature briquettes production. Results showed that xylene activated the pitch and gave it good cohesiveness to bind coke breeze at room temperature. The α, β and γ components were stimulated to have a high activity and the chemical structure of the pitch was changed, which resulted in activation of the pitch cohesiveness. After curing in air at 370 °C for 30 min and then carbonizing without special protection at 600 °C for 30 min, the pitch is transformed into pitch coke whose C–C bridge was capable of firmly binding the coke breeze particles and the strength of the briquettes reached 50.45 MPa, twice that of metallurgical coke. The process was more efficient and more economical than traditional processes.

1. Introduction

Coke is produced from selected metallurgical coals pyrolyzed at 1000 °C for 16–36 h [1,2]. The long and costly production process along with strict environmental regulations makes the coke commodity. The demand for coke is continuously increasing with the development of the metallurgical industry. It is necessary to save coke and search for substitutes for coke. Coke breeze, the by-product in coke production is unable to meet the requirement of the metallurgical industry because of its small particle size. It is usually dealt at a low price or even just stacked, which causes a huge waste of energy resources and a severe environment burden. Therefore, using coke breeze as raw material to produce metallurgical briquettes is of important significance to increase its value, saving metallurgical coke resources and protecting the environment [3–5].

A variety of production processes of metallurgical quality briquettes from coke breeze have been reported, but few of them have been adopted in industry. As alternatives to conventional coke, anthracite fuel briquettes including coke breeze and coal tar acid resin have been developed, but their strength has not met the requirement of the foundry cupola [4]. Raw coal with high volatile matter as the only raw material was used to produce high quality briquettes as a substitute for coke in the blast furnace, but the significant weight loss (30%–60%) and high carbonization temperature made them uneconomical [5–7]. Similarly, lignin or phenolic resin as a binder was used for the production of metallurgical quality briquettes [8–13], and briquettes with mechanical strength of 70 MPa were produced, but the high price of the binders was still a serious shortcoming, hindering the industrial application of the technologies.

Coal tar pitch with the advantages of low price, lower impurity content and the same elementary composition as coke is the most commonly used binder for the production of briquettes from coke breeze. However, coal tar pitch has little cohesiveness before being heated to melting state and the carbonization must be operated at high temperature, which makes the process complicated [5,13–17]. Ford [9,18,19] used methyl ethyl ketone to activate reactive sites on the carbon particles and make the carbon particles react with the polymer such as styrene by forming the reaction mixture into briquettes and then curing the briquettes. The briquettes are occasionally shown to be unsuitable as a coke substitute, but the method in which the activating reagent is used to promote the reactivity can be referenced.

In this paper, xylene was used to activate the cohesiveness of the pitch and make it to bind the coke breeze to form briquettes at room temperature. The binding state and the structure of the pitch were analyzed and thermal behavior of pitch and the briquettes was investigated. The work shows that the coke breeze could be bound into a firm briquette and the metallurgical briquettes were produced after heat treatment at low temperatures for short time (only 370 °C for 30 min and then 600 °C for 30 min). The briquettes could be carbonized under air or reducing atmosphere and even the hot waste gas of the blast furnace could be used to complete the carbonization process. The strength of the metallurgical briquettes is about 50 MPa, twice that of metallurgical coke and the process is more efficient and more economical [8,9]. The

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strength meets the requirement of the blast furnace and it will be further improved with temperature increase after feeding into the blast furnace.

2. Experimental

As illustrated in Fig. 1, the whole briquettes production process involves mixing the coke breeze with the pitch, dispersing of xylene in water, blending them with the mixture of the coke breeze and the pitch, briquetting the final blending material, curing the green briquettes, carbonizing the cured briquettes and measuring the strength of the briquettes.

2.1. Coke breeze

A common coke breeze is provided by a steel plant of China. As listed in Table 1, the coke breeze has a low content of volatile matter (1.44%) and its fixed carbon is up to 86.47% which leads to its high heat value. The particle size distribution comes out to be 96.86% of −3 mm and 29.63% of −0.5 mm, which indicates that the sample is favorably fine grained for briquetting. The investigation of J.W. Taylor et al. [20,21] showed that the amount of binder to cover the entire surface of the particles was found to be small and the strength of the briquettes was weak when there were a certain amount of coarser particles. In A. Benk's [9–13] study on the possibility of producing metallurgical quality briquettes from coke breeze, the coke breeze was entirely ground to −1 mm. This inevitably makes the process complicated and costly.

In this study, the original coke breeze was directly adopted to make briquettes without regrinding. To stabilize the size distribution of the samples, coke breezes of different size ranges were proportioned according to Table 1 for each test.

2.2. Coal tar pitch and xylene

Coal tar pitch is a by-product in the production of coke. The pitch exists as glass-like solid which gradually softens to a liquid state with increasing temperature [13–16]. In this research, a common coal tar pitch is directly utilized to research the production of metallurgical quality briquettes.

The properties of coal tar pitch used in this study are listed in Table 2. Volatile matter is up to 73.41% in the pitch while its ash content is only 0.08%. Its softening temperature is 67 °C, and the contents of C, H, N and O are 92.64%, 4.529%, 0.977% and 4.529% respectively. The research of Coban and Khramenko et al. [16,22] showed that the best pitch binder has a low softening temperature and high carbon content. According

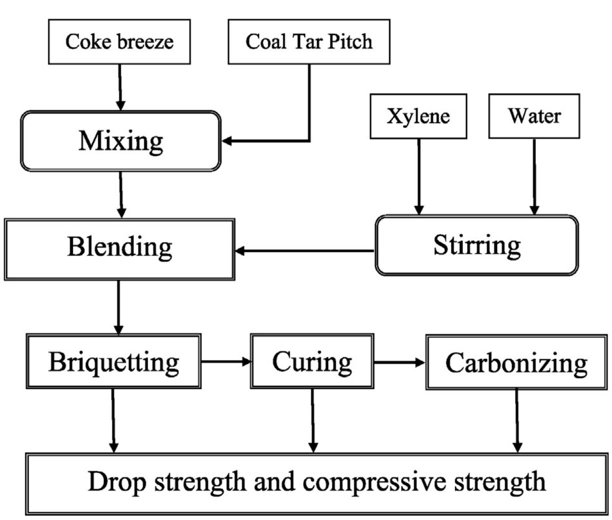

Fig. 1. Scheme of formed coke briquette production process.

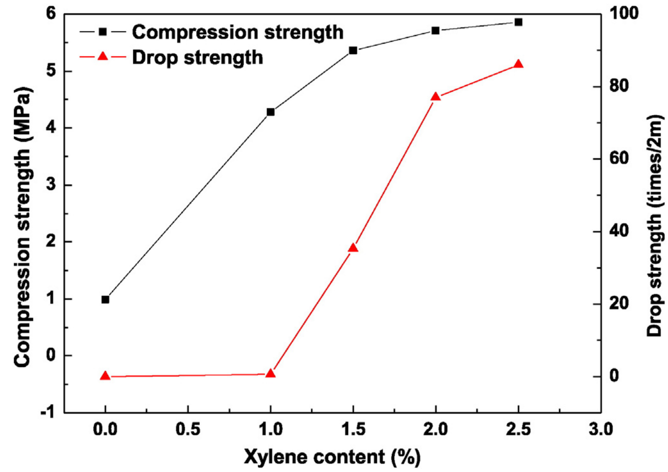

Fig. 2. Effect of xylene proportion on binding behavior of coal tar pitch.

to their finding, the pitch used in our research is a high quality binder. After preliminary test, the pitch optimum amount was found to be about 13% w/w of the coke breeze. Therefore, this pitch percentage was kept constant throughout this research.

The pitch exists in solid state at room temperature and it has little cohesiveness before heating to liquid state, which means that it can't bind coke breeze to form briquettes at room temperature. In order to make the pitch have high cohesiveness in the briquetting, it should be heated into liquid state before blending and briquetting and be kept hot until briquetting is finished. The heating requirement not only makes the process complicated and difficult to control but also increases the cost. With regards to this problem, we examined many different kinds of reagents and finally found xylene to be a cheap liquid compound and to be effective in activating the pitch into good cohesiveness at room temperature.

2.3. Blending and briquetting

Sampling was carried out carefully in order to be representative as much as possible. Then the coke breeze sample was dried under the sun and the pitch was ground to −0.5 mm. In the blending process, the coke breeze and the pitch were weighted and mixed gently until all of the coke particles were covered by the pitch. Then a certain amount of xylene was added to water whose proportion was 13% w/w of the coke breeze, and stirred until both were fully immersed in the physical form. The stirred liquid was added in the mixture of the coke breeze and the pitch, and mixed into a final blend for briquetting. In the briquetting process, each briquette was made by pressing 10 g of the blend in a 20.0 mm internal diameter steel mold at a pressure of 60 MPa for about 10 s with a closely fitting steel plunger under a hydraulic press machine.

2.4. Curing and carbonization

It is necessary for most of the production of metallurgical quality briquettes that the green briquettes are cured and then carbonized to achieve high strength. The curing and the carbonization processes usually require high temperature and long time, which is not efficient and uneconomical. Therefore, a new heat treatment process with low temperature and short time was developed with addition of xylene. All of the green briquettes were cured at 370 °C and a gentle gas flow of 0.5 L/min was adopted to pass through the briquettes. After curing for 30 min, the briquettes were taken out of the oven, cooled at room temperature and some of them were taken for strength measurement. Meanwhile, the rest of the cured briquettes were carbonized at higher