Research article

Semi-coke as solid heat carrier for low-temperature coal tar upgrading

Xiao-Hong Li, Jiang-Shan Ma, Li-Li Li, Bao-Fu Li, Jie Feng, William Turmel, Wen-Ying Li *

[a] Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education and Shanxi Province, Taiyuan 030024, China
[b] Training Base of State Key Laboratory of Coal Science and Technology Jointly Constructed by Shanxi Province and Ministry of Science and Technology, Taiyuan 030024, China

ARTICLE INFO

ABSTRACT

This paper focuses on the catalytic effect of semi-coke used as a heat carrier in the cracking of coal-tar from Shendong long-flame coal (SD) pyrolysis. Firstly, semi-cokes pyrolyzed from four different coals were chosen as investigative samples and quartz sand as their reference. The experiments were conducted in a fixed-bed re-actor under atmospheric conditions. Results show that the four semi-cokes have a catalytic cracking effect on vol-atile components. Compared with quartz sand, the tar yield of SD pyrolysis with semi-cokes decreases and the gas yield and light oil fractions in tar increase. The catalytic cracking effects of semi-cokes are relative to its phys-ical properties and inorganic species, and the latter has greater impact than the former. Secondly, recycling exper-iments were conducted to study the stability of SD semi-coke as a cracking catalyst. The products' distribution, gas composition, and the gasification reactivity of the semi-coke change little during the recycling of SD semi-coke, meaning that SD semi-coke is relatively stable. Lastly, SD semi-coke was selected as a heat carrier to inves-tigate its catalytic activity in a rapid heat transfer process similar to a practical operation. Compared with quartz sand, the catalytic cracking effect still exists in pyrolysis with hot SD semi-coke but a higher tar yield and a lower n-hexane soluble is obtained, indicating thermo-cracking contributes to more products than catalytic cracking.

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1. Introduction

Pyrolysis is an effective method to convert low rank coal to oil under mild conditions and can produce various products with extensive uses [1,2]. Compared with pyrolysis using traditional heating methods, py-rolysis through solid heat carriers has a higher efficiency of heat utiliza-tion. Coal can be heated more quickly and evenly, which is of great benefit to coal-tar upgrading [3–5]. Moreover, when the volatiles of py-rolysis spread in a gas phase, they will come in contact with solid heat carriers and the solid heat carriers will, except for the role of heat trans-fer, influence the secondary reactions of the volatiles (Fig. S1). The sec-ondary catalytic cracking of coal pyrolysis primary products is an efficient way to improve the quality of coal-tar and gas [6–8]. The solid heat carriers used in typical pyrolysis technologies included sand, semi-coke, and hot ash [5,9–13]. Some heat carriers, such as olivine [14] and FCC (fluid catalytic cracking catalyst) [15], may have a catalytic effect of improving the quality of coal-tar and gas.

Semi-coke produced simultaneously with coal-tar during pyrolysis can be used as a solid heat carrier, which has strong economic and prac-tical flexibility. Moreover, the porous textural structure of semi-coke can provide abundant active surfaces for tar cracking to improve the

quality of tar [16–18]. The good decomposing activity also relates to al-kali and alkaline earth metallic (AAEM) species, and transition metals in semi-coke. In addition, it is unnecessary for the regeneration of semi-coke, because semi-coke can be gasified or burned even if there is "addi-tional carbon" deposited on the semi-coke surface. Han et al. [19] stud-ied the catalytic effects of semi-coke on pyrolysis of Fugu coal in a two-stage fixed bed reactor. The results of which showed an increase of light components content (boiling point below 360 °C). They also found that the catalytic activity of metal that impregnated semi-coke was higher. Milne et al. [20] demonstrated that choosing semi-coke with sufficient active sites and proper conditions could maintain good catalytic activity for coal-tar reduction. While, there were also some reports about the in-fluence of semi-coke properties on its catalysis. Wang et al. [21] found that semi-coke treated by steam showed a much better catalytic perfor-mance for tar reduction than raw semi-coke, which was mainly attribut-ed to the fact that it had a larger surface area and more metal species were exposed on its surface. The study of Zeng et al. [22] also showed that the higher the specific surface area of semi-coke, the lower the tar content in the gas after catalytic reforming by semi-coke and the ox-ides of Na, Mg, Ca, and Fe could increase the activity of semi-coke for tar removal. Liu et al. [23] studied the catalytic cracking activity of semi-coke in different states through a two-stage reactor. Results showed hot semi-coke had a higher ability of catalytic cracking of tar compared with cool semi-coke, because the former had a larger specific surface area and more micropores. Gilbert et al. [24] also found that the hot semi-coke bed could promote tar reduction, especially by thermal cracking.

* Corresponding author at: Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education and Shanxi Province, Taiyuan 030024, China.
E-mail address: ying@tyut.edu.cn (W.-Y. Li).

Although much research on the catalytic effect of semi-coke has been done, there were few reports on the catalytic effect of semi-coke used as a heat carrier and the source of this effect. Besides, the recycling property of semi-coke used as a decomposing catalyst is another important factor. In this paper, four different semi-cokes were chosen to investigate the catalytic effects on tar quality. The recycling experiments of Shendong semi-coke were also conducted to study its catalytic stability. Finally, considering practical production, we simulated the pyrolysis using Shendong semi-coke as a heat carrier to investigate the influence of heat transfer on the catalytic activity of semi-coke.

2. Experimental

2.1. Coal sample

The coal used is Shendong long-flame coal (SD). Table 1 shows the proximate and ultimate analysis of this coal. The SD sample was crushed and screened into a diameter range of 1.18–2.00 mm. It was then dried at 110 °C in an oven for 12 h prior to the test.

2.2. Semi-coke heat carrier preparation

The catalytic effect of semi-coke is strongly relative to its physical structure, the contents and composition of minerals in the coal. Four different semi-cokes were chosen to investigate the catalysis of semi-coke during lower-temperature coal pyrolysis and quartz sand was chosen as its reference. The proximate and ultimate analysis of semi-coke heat carriers are list in Table 1. The quartz sand (QS) is commercially available and its diameter was 1.18–2.00 mm. Shendong semi-coke (SDC) and Jincheng semi-coke (JCC) were respectively products of the pyrolysis of SD and JC. The coal was pyrolyzed at 650 °C for 30 mins and further heated at 800 °C for 30 mins under a nitrogen gas flow. The Shenmu semi-cokes (SMC1 and SMC2), which are commercially available, were crushed, screened into diameters of between 1.18–2.00 mm, and then preheated similar to how SDC was processed.

Shendong semi-coke-ash free (SDC-AF) was made as follows: 100 g SDC was mixed with 1000 mL of 6 mol·L^{-1} HCl solution. The mixture was stirred at 60 °C in water bath for 1 h. After being filtered, HCl-washed SDC was treated with 1000 mL of HF (40%) in the same way. The sample was then washed by HCl again. The acid (HCl–HF–HCl) washed SDC was then washed with boiling deionized water until the pH value of the filtrate was near 7 and no chloride ions were detected by AgNO$_3$ in the filtrate. The sample was then dried at 110 °C for 24 h prior to the test.

2.3. Experimental apparatus and process

The pyrolysis experiments of SD were carried out in a reaction system which consisted of a lab-scale, fixed-bed reactor, a temperature controller, and a condensation unit [25,26]. Two modes of pyrolysis were designed in this study. The diagrammatic sketch of two modes is shown in Fig. S2. In Mode 1, the coal sample was heated externally

together with different semi-cokes or QS, in which the semi-cokes were not used as heat carriers because our main aim is to study the catalytic activity of different semi-cokes. Mode 1 was conducted as follows: the weight-bulk ratio of coal/semi-coke was 1/3 and was mechanically mixed. When the temperature of the heating furnace reached 650 °C, about 40 g of mixture (coal and semi-coke) was fed into the reactor and placed under flowing nitrogen gas for 10 mins to exclude the air. Then the sample was put into the furnace and pyrolyzed for 30 mins under a nitrogen gas flow of 100 mL·min^{-1}. Liquid products were condensed when flowing through a cold trap (−20 °C) and gas was collected by a gas bag. After pyrolysis, the semi-coke was cooled and weighed. Liquid products were washed out from the cold trap by tetrahydrofuran and treated through vacuum distillation by a rotary evaporator at 40 °C to collect the tar. Gas yield was obtained by difference. In this paper, the n-hexane soluble content of tar was regarded as the indicator of tar quality. Moreover, the recycling experiments of SDC were conducted after each pyrolysis experiment, part of the semi-coke was treated at 800 °C for 30 mins for the subsequent experiment. During this process, the recycled samples were marked as semi-coke1, semi-coke2, and semi-coke3.

Experiments that simulate the pyrolysis by solid heat carrier were conducted in Mode 2 as follows: the SD semi-coke heat carrier was first fed into the reactor and heated to 800 °C. The coal sample was then fed into the shaking reactor, mixed with the hot heat carrier and pyrolyzed for 3 mins. The coal sample was heated internally by hot SDC or QS in these experiments. The collection and analysis of products were the same as those of Mode 1.

2.4. Calculation of the product yields

The product yields are calculated as follows:

Semi-coke yield $Y_c = M_c/M$

Tar yield $Y_T = M_T/M$

Water yield $Y_W = (M_L - M_T)/M$

Gas yield $Y_G = 1 - Y_C - Y_T - Y_W$

n−hexane soluble/tar $f_{N/T} = (M_T - M_{NI})/M_T$

where M, M_C, M_T, M_L and M_{NI} are the mass of SD coal sample, semi-coke, coal-tar, liquid product; and n-hexane-insoluble portion, respectively. All of the above calculations were based on an air-dry basis. All pyrolysis experiments were carried out at least three times and the arithmetical averages were calculated for all the results.

2.5. Analysis and characterization

The composition of pyrolysis gas, including the components H_2, CH_4, CO, CO_2, and N_2 (carrier gas), was analyzed with a GC-950 gas chromatograph.

The simulated distillation of tar was conducted on a HCT-1 thermogravimetric analyzer (TGA) under a nitrogen flow of 40 mL·min^{-1}. The samples were heated from ambient temperature to 400 °C at the rate of 5 °C·min^{-1}. We divided the tar fractions into 5 parts by temperature ranges in TG: <110 °C, 110–140 °C, 140–180 °C, 180–240 °C, and higher than 240 °C. The classification was based on the calibration curve using model compounds with real boiling points of: <180 °C, 180–230 °C, 230–300 °C, 300–400 °C, and higher than 400 °C, see Fig. S3. Tar is composed of more than 500 known constituents, which means azeotropes may exist in coal tar and lead to deviations in simulated distillation. For example, pyridine–phenols azeotrope has a higher boiling point than each pure component (negative azeotrope), while pyridine–toluene azeotrope has a lower boiling point than each pure component

Table 1
Property of coal and semi-coke heat carrier.

Sample	Proximate analysis (wt.%, ad)				Ultimate analysis (wt.%, daf)				
	M	V	A	FC	C	H	O[a]	N	S
SD	6.38	6.85	29.80	56.97	80.49	4.34	13.52	1.23	0.41
JC	1.07	6.13	25.42	67.38	87.94	3.22	5.32	1.10	2.42
SDC	2.38	5.75	15.13	76.74	89.71	2.43	6.74	0.85	0.27
JCC	0.68	0.36	21.49	77.47	94.40	0.74	3.84	0.51	0.51
SMC1	2.81	7.59	35.49	54.11	90.06	1.36	6.55	1.31	0.72
SMC2	2.57	4.98	8.31	84.14	91.90	1.26	5.24	1.31	0.29

[a] By difference; M—moisture; A—ash; V—volatiles; FC—fixed carbon; ad—air dry basis; daf—dry ash-free basis.